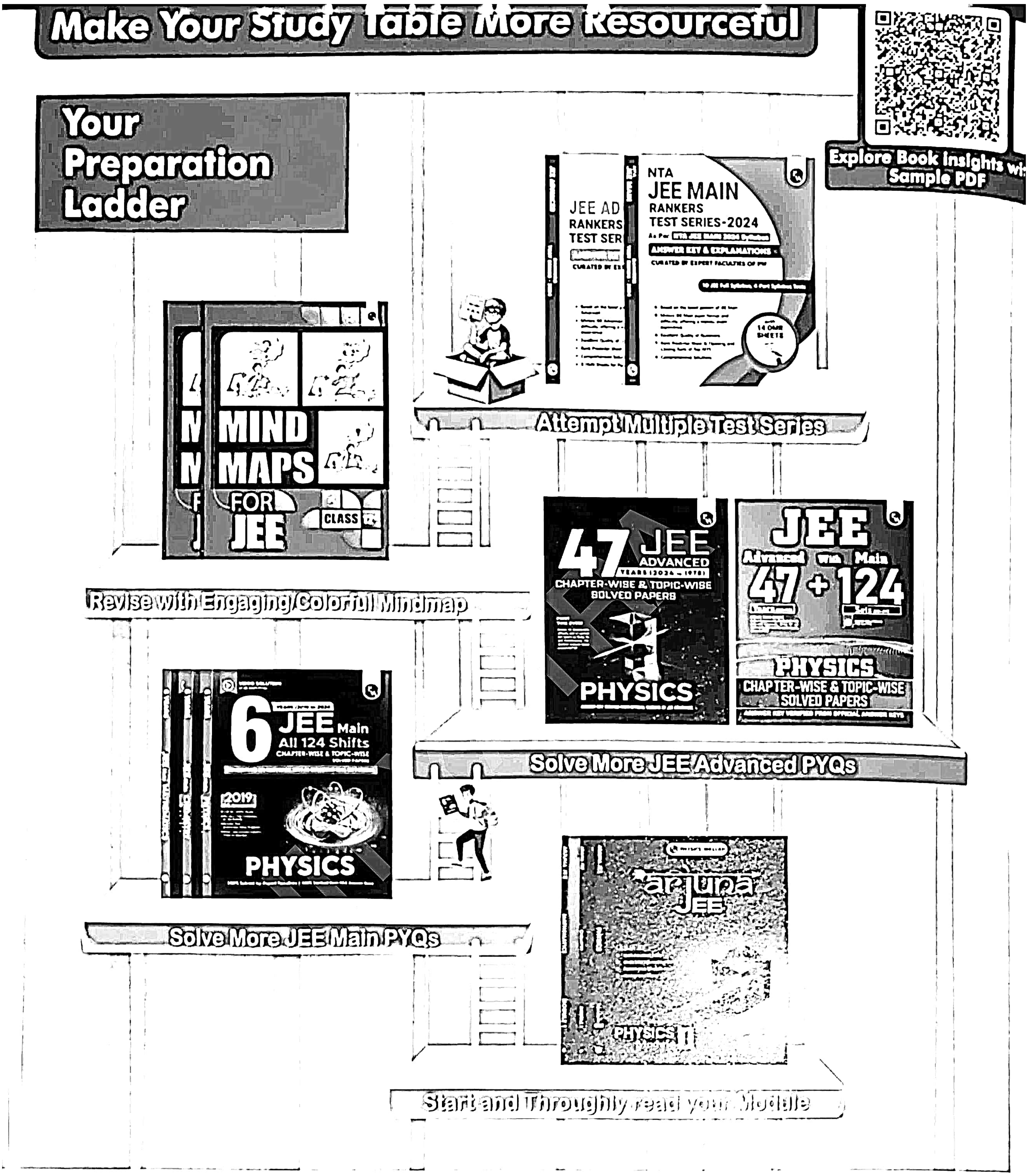
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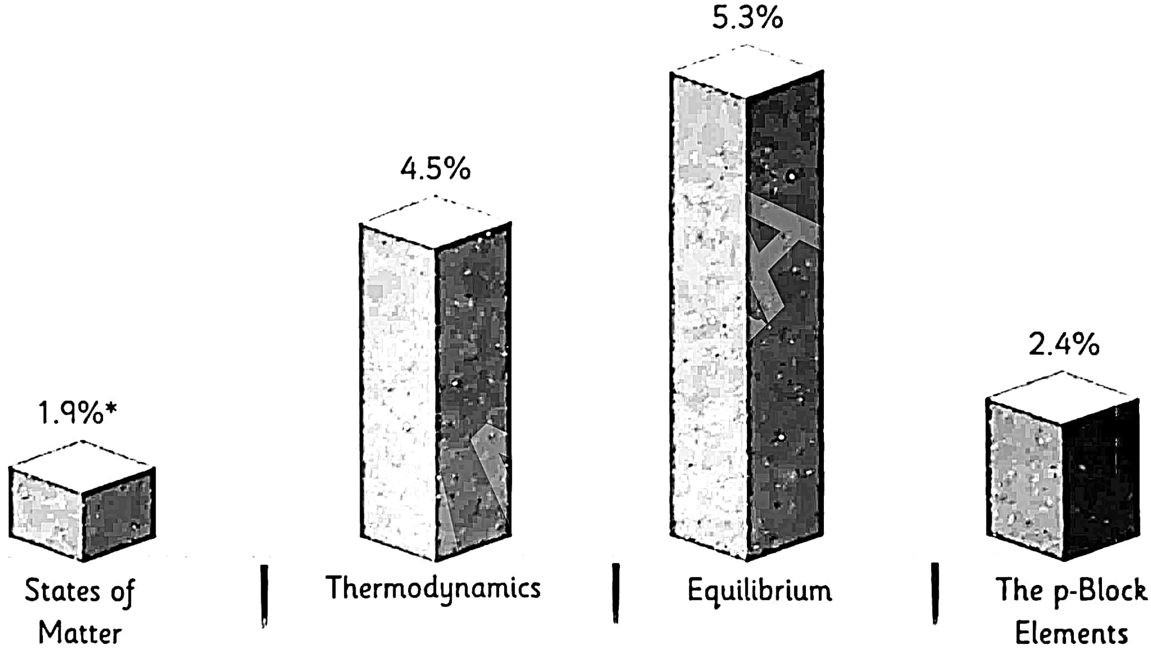

Chapter Wise Weightage (in %) Based on Past 6 Years JEE Main Papers

**Chapter-States of Matter has been deleted from the recent syllabus of JEE Main. The provided Chapter-wise weightage is based on the past five years (2023-2019) PYQs for your reference.*

CHEMISTRY
Module 2

Mindfulness: In this module for the emotional well being we will practice Mindfulness along with our regular academic learning

Credit:--- Divansh.....

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PREFACE

A dedicated team at Physics Wallah (PW) works diligently to provide students with quality content for the JEE exam.

From the beginning, the whole content team comprising Academic faculties, DTP operators, Proofreaders and others are involved in shaping the material to their best knowledge and experience to produce powerful content for the students.

Faculties have adopted a new style of presenting the content in easy-to-understand language and have provided the team with their guidance and supervision throughout the creation of this Study Material.

Physics Wallah (PW) strongly believes in conceptual and fun-based learning. PW provides exam-focused content designed to offer clarity and value to students.

A plethora of **JEE Study Material** is available in the market but PW professionals are continuously Working to provide comprehensive study material for our **JEE** students.

This Study Material adopts a multi-faceted approach to master and understanding the concepts by having a rich diversity of questions asked in the examination and equip the students with the knowledge for this competitive exam.

The main objective of the study material is to provide a large number of quality problems with varying cognitive levels to facilitate the teaching learning of concepts that are presented through the book.

It is widely used by aspirants because of its easy-to-understand language and clear illustrations with diagrams, mnemonics, flow charts and tables.

Students can benefit themselves by attempting the exercises given in this Study Material for the self-assessment and also mastering the basic techniques of problem solving.

The questions are entirely designed in accordance with the exam relevant topics that helps to develop examination temperament within the students.

By mastering the Physics Wallah (PW) study material curated by the PW team, students can improve their chances of qualifying for the JEE exam and achieving a strong rank.

In each chapter, for better understanding, questions have been classified according to the latest syllabus of JEE:

- The nature and diversity of the questions help students to ace the examination
- Quality questions to strengthen the concept of the topic at the zenith level.

BOOK FEATURES

- Detailed theory with Train Your Brain and Concept Application Questions
- "Garuda" Section for Solved Miscellaneous Examples
- School Level Problems for School Going Students
- "Brahmastra" Section for Revision, "Pratham" Section for JEE Main Level and "Parikshit" Section for Advance Level MCQs covered in exercises
- Match the Column, Comprehension Based, Numerical Type and Multicorrect questions covered for complete practice
- JEE Past Year Questions
- PW Challengers Problems for Difficult Level Questions
- Elaborated Solutions Booklet you can get separately

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3P PROGRESSOR

PLANNER

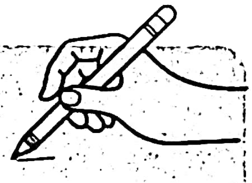
CHAPTER NAMES	Start Date of Module	End Date of Module	Solve More PYQs	Revision Period	Re-revision Period (Before Test Series)
States of Matter					
Thermodynamics					
Equilibrium					
The p-Block Elements					

PROGRESS TRACKING

CHAPTER NAMES	Solved Examples	School Level	Topicwise	Main Level	Advanced Level	PYQs	Challengers
States of Matter	☐	☐	☐	☐	☐	☐	☐
Thermodynamics	☐	☐	☐	☐	☐	☐	☐
Equilibrium	☐	☐	☐	☐	☐	☐	☐
The p-Block Elements	☐	☐	☐	☐	☐	☐	☐

PREP POINTERS

Note down the topic you want to revise or section you want to re attempt while your preparation.



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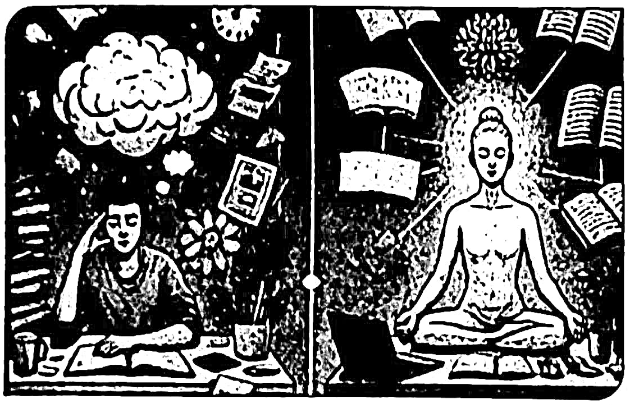
The Power of Mindfulness: Your Key to Limitless Potential

"Mindfulness is about being fully present and aware of your thoughts and actions. For a JEE aspirant, it means focusing on the present moment, letting go of distractions, and managing stress. Practicing mindfulness enhances clarity, improves concentration, and fosters emotional balance, helping you navigate challenges with calm and purpose"

> *"Do not dwell in the past, do not dream of the future, concentrate the mind on the present moment."*
> **– Buddha**



Without Mindfulness

- ❖ Constant multitasking and stress lead to overwhelm, making it hard to focus or retain information.
- ❖ Pushing beyond limits without awareness causes exhaustion, burnout, and reduced performance.

With Mindfulness

- ❖ Focusing fully on the task enhances understanding and retention of complex concepts. Mindful breaks help recharge, boosting energy and productivity.
- ❖ Managing emotions through mindfulness promotes calm decision-making and reduces stress.

SCENARIOS

Without Mindfulness		*With Mindfulness*
Feeling overwhelmed and doubting your abilities.	After a Difficult Mock Test	Viewing it as a learning opportunity to identify weak areas and improve.
Taking criticism personally and feeling discouraged.	Feedback from a Teacher	Accepting feedback constructively and using it to refine your preparation.
Burning out, losing focus, and feeling frustrated.	Studying Long Hours	Taking regular breaks, staying focused, and enjoying the process of learning.
Getting stuck, feeling frustrated, and giving up too quickly.	Facing a Tough Concept	Breaking it down into smaller steps, seeking help, and persisting patiently.
Feeling inadequate or overly competitive, leading to stress.	Comparing Scores with Friends	Understanding that everyone's journey is unique and focusing on personal growth.
Feeling regretful, isolated, and distracted.	Missing a Social Event for Study	Acknowledging the temporary sacrifice and reminding yourself of the long-term rewards.
Feeling anxious and losing motivation.	Unexpected Challenges During Preparation	Viewing challenges as opportunities to develop resilience and problem-solving skills.
Feeling monotonous and uninspired, leading to procrastination.	Daily Study Routine	Staying grateful for the opportunity to learn, making the routine engaging, and celebrating small achievements.

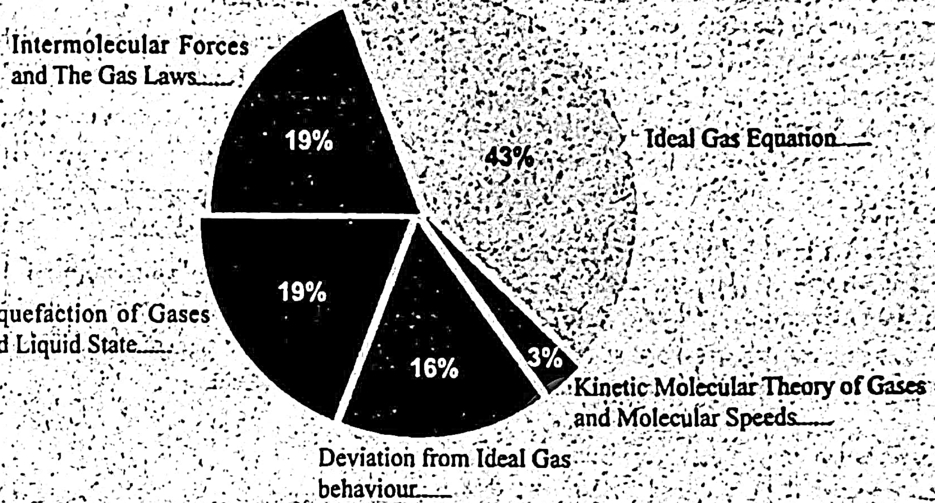
This demonstrates how adopting a mindset of **Mindfulness** can help students navigate the stresses and challenges of exam preparation with more resilience and positivity. It highlights how a shift in perspective can transform obstacles into opportunities for growth and improvement.

CHAPTER

6

States of Matter

Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)*



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

**This chapter has been deleted from the recent syllabus of JEE Main. The provided topicwise analysis is based on the past five years (2023-2019) PYQs for your reference.*

INTRODUCTION

Matter as we know broadly exists in three states.

There are always two opposite tendencies between particles of matter which determine the states of matter.

- Inter molecular attractive forces.
- The molecular motion / Thermal motion of particles.

Matter

Properties	**Solid state**	**Liquid state**	**Gaseous state**
Attractive force	• Strong	• Weak	• Almost zero
Thermal motion	• Almost zero	• Greater	• Random motion
Volume	• Fixed volume	• Fixed volume	• Varies with container
Geometry	• Definite	• Not definite	• Not definite

In this chapter the properties and behaviour of the gases will be analysed and discussed in detail. These properties are measured with the help of the gas laws as proposed by Boyle, Charles, Gay Lussac etc.

INTERMOLECULAR FORCES

Intermolecular force are the forces of interaction between particles (atoms and molecules).

Dispersion Forces or London Forces

- Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules.
- The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also.

Credit:--- Divansh.....

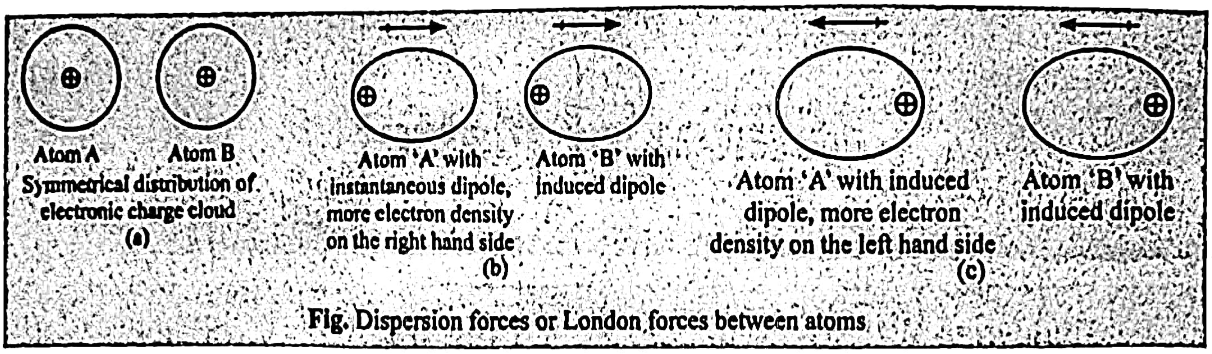
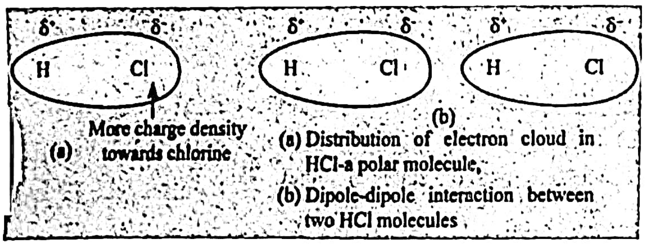

Atom A
Atom B
Symmetrical distribution of electronic charge cloud
(a)
Atom 'A' with instantaneous dipole, more electron density on the right hand side
Atom 'B' with induced dipole
(b)
Atom 'A' with induced dipole, more electron density on the left hand side
Atom 'B' with induced dipole
(c)

Fig. Dispersion forces or London forces between atoms

- These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$)
- These forces are important only at short distance (~500 pm) and their magnitude depends on the polarisability of the particle.

Dipole–Dipole Forces

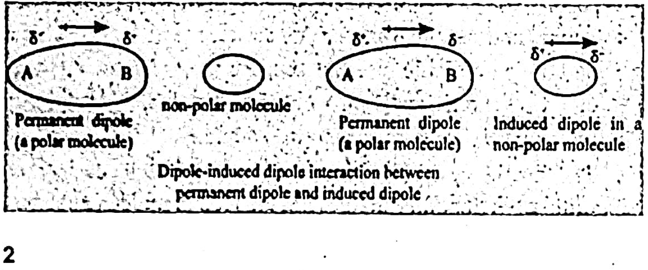
- Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess "partial charges" and these charges are shown by Greek letter delta (δ).
- This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.
- Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $1/r^6$,


δ+
δ−
H
Cl
More charge density towards chlorine
(a)
(b)

(a) Distribution of electron cloud in HCl-a polar molecule,
(b) Dipole-dipole interaction between two HCl molecules

Dipole–Induced Dipole Forces

- This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole.
- Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud.
- In this case interaction energy is proportional to $1/r^6$.
- Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.


δ+
δ−
A
B
Permanent dipole (a polar molecule)
non-polar molecule
Permanent dipole (a polar molecule)
Induced dipole in a non-polar molecule

Dipole-induced dipole interaction between permanent dipole and induced dipole

Hydrogen Bond

- This is found in the molecules in which highly polar N–H, O–H or H–F bonds are present.
- Energy of hydrogen bond varies between 10 to 100 kJ mol^{-1} therefore, hydrogen bonds are powerful force in determining the structure and properties of many compounds, for example proteins and nucleic acids.
- Strength of the hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of other molecule.

$$\overset{\delta+}{H}-\overset{\delta-}{F}\ldots\overset{\delta+}{H}-\overset{\delta-}{F}$$

PHYSICAL PROPERTIES OF THE GASEOUS STATE

(i) Gases or their mixtures are homogeneous in composition.
(ii) Gases have very low density.
(iii) Gases have infinite expansibility and high compressibility.
(iv) Gases exert pressure.
(v) Gases possess high diffusibility.
(vi) Gases can be liquefied by cooling under high pressure.
(vii) Gases undergo similar change with the change of temperature and pressure. This behaviour of gases is governed by certain laws known as gas laws.

Measurable Properties of Gases

(i) **Mass:** Mass in gm = Number of Moles × Molecular mass.
(ii) **Volume:** Volume of the gas is the volume of container in which they are filled in.
(iii) **Temperature:** Temperature of a gas is the measure of kinetic energy of gas.

$$\text{Kinetic energy} \propto \text{Temperature}$$

(iv) **Pressure:** Pressure of gas is defined as the force exerted by the gas on the walls of its container. It is often assumed that pressure is isotropic, i.e. it is the same in all the three directions.

Credit:--- Divansh.....

Key Note

- 1 atm = 1.013×10^5 N/m^2 = 1.013×10^5 Pa = 1.013 bar = 760 torr = 76 cm Hg = 760 mm Hg
- 1 bar = 10^5 N/m^2 = 100 kPa
- 1L = 1dm^3 = 10^{-3} m^3
- 1L–atm = 101.325 J
- **Atmospheric pressure:** The pressure exerted by atmosphere on earth's surface at sea level is called 1 atm.

THE GAS LAW

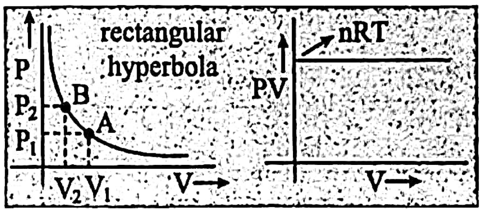
Boyle's Law

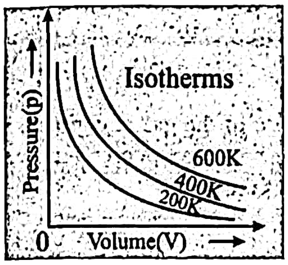
For a fixed amount of gas at constant temperature, the volume occupied by the gas is inversely proportional to the pressure applied on the gas (or pressure of the gas).

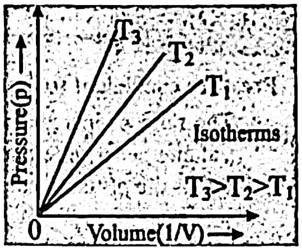
$$V \propto \frac{1}{P} \text{ (at constant T and n)}$$

Hence PV = constant (k) $\Rightarrow P_1V_1 = P_2V_2 = \ldots = nRT$

(Here k = nRT)







Key Note

- A relationship can be obtained between density and pressure of a gas by using Boyle's law:
- Density 'd' is related to the mass 'm' and the volume 'V' by the relation $d = \frac{m}{V}$.
- From Boyle's law equation, we obtain the relationship.

$$d = \left(\frac{m}{k}\right) p = k'p$$

- This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

Train Your Brain

Example 1: A gas is initially at 1 atm pressure. To compress it to 1/4 th of initial volume, what will be the final pressure required?

Sol. $P_1 = 1$ atm $\quad V_1 = V$

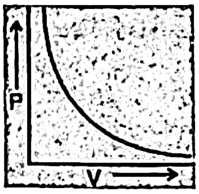
$P_2 = ? \quad V_2 = \frac{V}{4}$

$P_1V_1 = P_2V_2$ at const. T & n

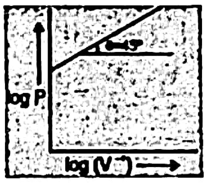
$$P_2 = \frac{P_1V_1}{V_2} = \frac{1\text{ atm} \times V}{\frac{V}{4}} = 4 \text{ atm}$$

Example 2: Which of the following curve does not represent Boyle's law?

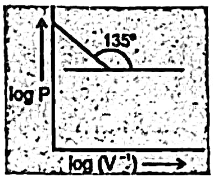
(*a*)



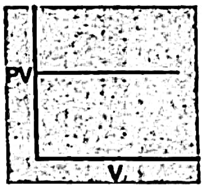
(*b*)



(*c*)



(*d*)



Sol. (*c*) PV = K

$$P = \frac{K}{V} = KV^{-1}$$

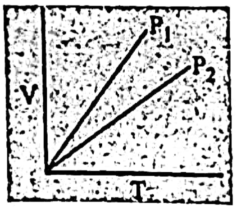
$\log P = \log K + \log V^{-1}$

It follows equation of straight line having positive slope & positive intercept when drawn between log(P) and log (V^{-1}).

Hence, option (*c*) is incorrect representation.

Concept Application

1. A 2.24 L cylinder of oxygen at 1 atm and 273 K is found to develop a leakage. When the leakage was plugged the pressure dropped to 570 mm of Hg. The number of moles of gas that escaped will be:
(*a*) 0.025 (*b*) 0.050 (*c*) 0.075 (*d*) 0.09
2. V versus T curves at constant pressure P_1 and P_2 for an ideal gas are shown in fig. Identify the correct option?



(*a*) $P_1 > P_2$ (*b*) $P_1 < P_2$
(*c*) $P_1 = P_2$ (*d*) All of these

Charles's Law

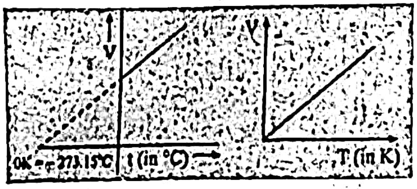
For a fixed amount of gas at constant pressure, volume occupied by the gas is directly proportional to temperature of the gas on absolute scale of temperature.

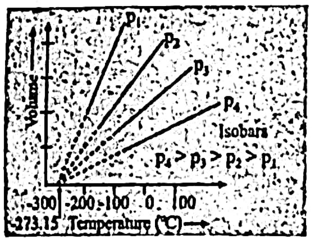
V α T or V = kT (at constant P & n)

$$\frac{V}{T} = \text{constant (k)}$$

$$\left[\text{Here } k = \frac{nR}{P}\right]$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \ldots = \frac{nR}{P}$$





- ❖ Since volume is proportional to absolute temperature the volume of a gas should be theoretically zero at absolute zero temperature.
- ❖ Infact no substance exists as gas at a temperature near absolute zero, though the straight line plots can be extrapolated to zero volume.
- ❖ By considering −273.15°C as the lowest approachable limit, Kelvin developed temperature scale which is known as absolute scale.

Key Note

Volume coefficient (α_v) of a gas:

- ❖ The ratio of increase in volume of a gas at constant pressure per degree rise of temperature to its volume at 0°C is the volume coefficient of the gas.

$$V_t = V_0(1 + \alpha_v t)$$

For all gases, $\alpha_v = \frac{1}{273}$ °C⁻¹

$$V_t = V_0 + \frac{t}{273.15}V_0$$

$$V_t = V_0\left(1 + \frac{t}{273.15}\right)$$

$$V_t = V_0\left(\frac{273.15 + t}{273.15}\right)$$

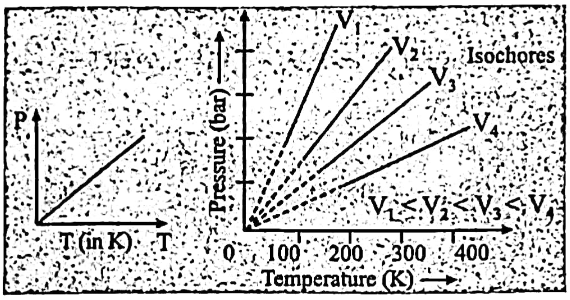
Gay-Lussac's Law

For a fixed amount of gas at constant volume, pressure of the gas is directly proportional to temperature of the gas on absolute scale of temperature.

P α T (at constant V ∝ n)

$$\frac{P}{T} = \text{constant (k)} \qquad \left(\text{Here } k = \frac{nR}{V}\right)$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$



Key Note

Pressure coefficient (α_p) of a gas:

- ❖ The ratio of increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at 0°C is the pressure coefficient of the gas.

$$P_t = P_0(1 + \alpha_p t)$$

For all gases, $\alpha_p = \frac{1}{273}$ °C⁻¹

Train Your Brain

Example 3: If the temperature of a particular amount of gas is increased from 27°C to 57°C. Find final volume of the gas, if initial volume = 1L and assume pressure is constant.

Sol. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{1}{(273+27)} = \frac{V_2}{(273+57)}\text{; So } V_2 = 1.1\text{L}$$

Credit:--- Divansh.....

Example 4: The temperature of a certain mass of a gas in a rigid container is doubled. If initially the gas is at 1 atm pressure. Find the % increase in pressure?

Sol. $\frac{P_1}{T_1}=\frac{P_2}{T_2};\frac{1}{T}=\frac{P_2}{2T}$

$$\% \text{ increase} = \frac{2-1}{1} \times 100 = 100\%$$

Example 5: The temperature of a certain mass of a gas was increased from 27°C to 37°C at constant volume. What will be the final pressure of the gas.

Sol. $\frac{P_1}{T_1}=\frac{P_2}{T_2};\frac{P}{300}=\frac{P_2}{310};P_2=\frac{31}{30}P$

Concept Application

3. If the pressure of a gas contained in a closed vessel is increased by 0.4% when heated by 1°C it's initial temperature must be:
   (*a*) 250 K (*b*) 250°C
   (*c*) 25°C (*d*) 25 K

Avogadro's Hypothesis

At constant pressure & temperature, equal number of molecules of different gases will occupy equal volume.

$V \propto n$ (at constant P & T)

i.e., $\frac{V}{n} = \text{Constant} = \left(\frac{RT}{P}\right)$

⇒ Volume occupied by one mole of each and every gas under similar conditions will be equal.

Key Note

- One mole of any gas or a combination of gases occupies 22.71098 L of volume at STP (1 bar and 0°C).
- The previous standard is still often used, and applies to all chemistry data more than decade old, in this definition **Standard Temperature and Pressure STP** denotes the same temperature of 0°C (273.15K), but a slightly higher pressure of 1 atm (101.325 kPa) when molar volume = 22.413996 L.
- **Standard Ambient Temperature and Pressure** (SATP), conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e. exactly 10^5 Pa). At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol^{-1}.

IDEAL GAS EQUATION

- Combining all the gas relations in a single expression which describes relationship between pressure, volume and temperature, of a given mass of gas we get an expression known as **ideal gas equation.**
- At constant T and n; $V \propto \frac{1}{P}$ **Boyle's Law**
- At constant p and n; $V \propto T$ **Charles' Law**
- At constant p and T; $V \propto n$ **Avogadro Law**

$$\Rightarrow V \propto \frac{nT}{P}$$

$$\Rightarrow V = R\frac{nT}{P}$$

$$\Rightarrow R = \frac{pV}{nT}$$

$$pV = nRT$$

Equation (pV = nRT) is called **ideal gas equation.**

$R = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$

$= 8.314$ J/Kmole ($\approx 25/3$) = 1.987 cal/K.mole (≈ 2)

$= 0.0821$ Latm/K/mole ($\approx 1/12$)

- If temperature, volume and pressure of a fixed amount of gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2 then we can write

$$\frac{P_1V_1}{T_1} = nR \quad \text{and} \quad \frac{P_2V_2}{T_2} = nR$$

$$\Rightarrow \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (equation of change of state)}$$

- This equation is also known as **Combined gas law.**

Key Note

- **Cylinder type** (thick skin) can withstand pressure difference till a limit but cannot have volume change.
- **Connecting containers having gases:** On removal of nozzel the gas from higher pressure will travel so as to have equal pressure at both the containers.... from idea of total moles & final temperature each parameter can be calculated.
- **Changes in open vessel:** Pressure of air remains constant & so is the volume.

  $\therefore n_1T_1 = n_2T_2$
- **Changes in closed vessel:** $\frac{P_1}{n_1} = \frac{P_2}{n_2}$

AMAGAT'S LAW OF PARTIAL VOLUME

According to this law at constant temperature and pressure, the total volume of mixture of gases which don't react is equal to the sum of partial volumes of each component present in mixture.

$$V_T = V_1 + V_2 + V_3 + \ldots\ldots$$

Partial Volume:

Partial volume of any component is defined as the volume occupied by that particular component measured under the given condition of pressure and temperature.

$PV = nRT$

$V \propto n$

Let us consider a mixture of three non-reacting gases A, B and C present in a container which have no. of moles n_A, n_B and n_C respectively. For each gas partial volume is

$$V_A = n_A\left(\frac{RT}{P}\right),\quad V_B = n_B\left(\frac{RT}{P}\right) \quad \text{and} \quad V_C = n_C\left(\frac{RT}{P}\right)$$

Total Volume:

$$V_T = V_A + V_B + V_C = (n_A + n_B + n_C)\left(\frac{RT}{P}\right) = n_T\left(\frac{RT}{P}\right)$$

RELATION OF DENSITY WITH IDEAL GAS EQUATION

$PV = nRT$

$$n = \text{number of moles} = \frac{\text{Amount of gas}}{\text{Mol. wt of gas}} = \frac{w}{M_0}$$

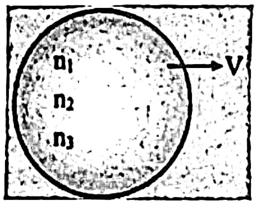
$$\Rightarrow PV = \frac{w}{M_0} \times RT$$

$$\Rightarrow \boxed{PM_0 = \frac{w}{V}RT = DRT} \qquad \boxed{\text{i.e., } D = \frac{PM_0}{RT}}$$

D = Density of gas

DALTON'S LAW OF PARTIAL PRESSURE

In a mixture of non reacting gases, partial pressure of any component of gas is defined as pressure exerted by that component if whole volume of mixture had been occupied by that component.



$$P_1 = \frac{n_1 RT}{V};\ P_2 = \frac{n_2 RT}{V};\ P_3 = \frac{n_3 RT}{V}$$

Total pressure = $P_1 + P_2 + P_3$.

Dalton's law: For a non reacting gaseous mixture, total pressure of the mixture is the summation of partial pressure of the different component of gases.

$$P_{Total} = P_1 + P_2 + P_3 = \frac{(n_1 + n_2 + n_3)RT}{V}$$

$\frac{P_1}{P_T} = \frac{n_1}{n_T} = X_1$ (mole fraction of first component of gas)

$\frac{P_2}{P_T} = \frac{n_2}{n_T} = X_2$ (mole fraction of second component of gas)

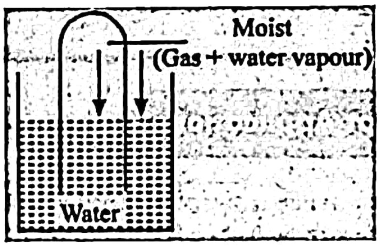
$\frac{P_3}{P_T} = \frac{n_3}{n_T} = X_3$ (mole fraction of third component of gas)

Key Note

- ❖ It has been observed that gases are generally collected over water and therefore are moist.

$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{water vapour}}$$

Pressure of dry gas = Pressure of moist gas – aqueous tension.



- ❖ The pressure exerted by water vapour is constant with water at a particular temperature and is called as aqueous tension, which varies directly with the temperature and becomes 760 mm Hg at 100°C.
- ❖ $\text{Relative Humidity}(R_H) = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$

Train Your Brain

Example 6: The partial pressure of hydrogen in a flask containing 2 grams of hydrogen and 32 gm of sulphur dioxide is

(*a*) 1/16th of the total pressure

(*b*) 1/9th of the total pressure

(*c*) 2/3rd of the total pressure

(*d*) 1/8th of the total pressure

Sol. (*c*) $n_{H_2} = \frac{2g}{2\,g/mol} = 1\,mol,\ n_{SO_2} = \frac{32g}{64\,g/mol} = 0.5\,mol$

$$\therefore P_{H_2} = \frac{n_{H_2}}{\left(n_{H_2} + n_{SO_2}\right)} \times P_T = \frac{1}{(1+0.5)} \times P_T = \frac{2}{3}P_T.$$

Example 7: Equal volume of two gases which do not react together are enclosed in separate vessels. Their pressures are 10 mm Hg and 400 mm Hg respectively. If the two vessels are joined together, then what will be the pressure of the resulting mixture (temperature remaining constant):

(*a*) 120 mm Hg (*b*) 500 mm Hg
(*c*) 1000 mm Hg (*d*) 205 mm Hg

Sol. (*d*) Let, vol of containers be V & temperature be T

$P_1 = 10$ mm Hg $\quad P_2 = 400$ mm Hg

$$\therefore \quad n_1 = \frac{P_1V}{RT} \quad \& \quad n_2 = \frac{P_2V}{RT}$$

$$\therefore \quad n_1 + n_2 = \frac{(P_1+P_2)\times V}{RT} \qquad \text{... (i)}$$

After joining two containers final volume = (V + V) = 2V (for gases)

$$\therefore \quad P_{\text{final}} = \frac{(n_1+n_2)RT}{V_{\text{final}}} = \frac{(P_1+P_2)\times V}{RT}\times\frac{RT}{2V}$$

$$= \frac{(P_1+P_2)}{2} = \frac{(10+400)\text{mm}}{2} = 205 \text{ mm Hg.}$$

Concept Application

4. Which of the following gas mixture has Dalton's law of partial pressure not applicable?
(*a*) SO_2 and Cl_2 (*b*) CO_2 and N_2
(*c*) CO and CO_2 (*d*) CO and N_2

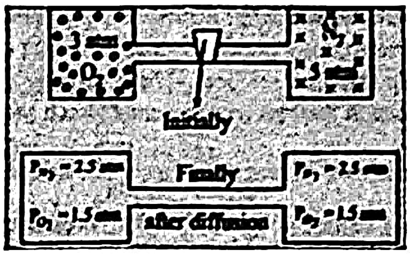
5. A 2.5L flask contains 0.25 mol each of SO_2 and CO_2 gas at 27°C. Calculate the partial pressure exerted by SO_2, CO_2 and total pressure respectively (in atm).
(*a*) 2.46, 2.46, 4.92 (*b*) 1.23, 2.46, 2.46
(*c*) 2.46, 1.23, 1.23 (*d*) None of these

6. 56 g of nitrogen and 96 g of oxygen are mixed isothermally at a total pressure of 10 atm. The partial pressures of oxygen and nitrogen (in atm) are respectively:
(*a*) 4, 6 (*b*) 5, 5
(*c*) 2, 8 (*d*) 6, 4

7. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is:
(*a*) $\frac{2}{3}$ (*b*) $\frac{1}{3}\times\frac{273}{298}$
(*c*) $\frac{1}{3}$ (*d*) $\frac{1}{2}$

GRAHAM'S LAW OF DIFFUSION/EFFUSION

Diffusion: Net spontaneous flow of gaseous molecules from region of high concentration (higher partial pressure) to the region of lower concentration or lower partial pressure. Flow will be from both sides, both gas will try to equalise its partial pressure in both the vessels respectively. e.g.



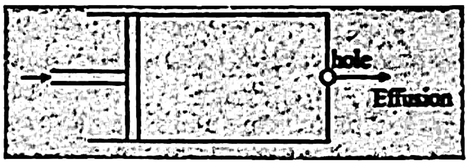
Graham's Law

At same pressure (partial pressure), the rate of diffusion of different gases is inversely proportional to square root of the density of different gases.

- Rate of diffusion, $r \propto \frac{1}{\sqrt{d}}$ {d = density of gas}

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \sqrt{\frac{(VD)_2}{(VD)_1}} \quad \text{(V.D is vapour density)}$$

- **Effusion:** (forced diffusion) a gas is made to diffuse through a hole by the application of external pressure.



- **Rate of diffusion and effusion can be termed as**

r = rate of change in pressure = $\frac{dP}{dt}$

r = volume flow rate = $\frac{dV_{out}}{dt}$

r = moles flow rate = $\frac{dn_{out}}{dt}$

r = distance travelled by gaseous molecules per unit time = $\frac{dx}{dt}$

- The general form of the graham's law of diffusion can be stated as follows, when one or all of the parameters are varied.

$$\text{rate} \propto \frac{PA}{\sqrt{TM}}$$

P – Pressure, A – area of hole, T – Temp., M – mol. wt.

$$r \propto P$$

$$r \propto \frac{1}{\sqrt{M}} \Rightarrow \boxed{\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}}$$

Key Note

Application of graham's law of diffusion in enrichment of isotopes:

Enrichment of Light component:

- If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas passing through will be enriched in lighter component by a factor $\sqrt{\frac{M_B}{M_A}}$, called

Credit:--- Divansh.....

enrichment factor because lighter molecules effuse more rapidly than heavier ones. The remaining gas will be enriched in the heavier component. Each passage gives an enrichment factor equal to $\sqrt{\frac{M_B}{M_A}}$ and so thousands of such barrier in succession are necessary to provide sufficient enrichment of heavier component.

- Thus, enrichment factor for first barrier or operation $f_1 = \sqrt{\frac{M_B}{M_A}}$
- Overall separation or enrichment factor $f = \frac{n'_A / n'_B}{n_A / n_B}$ where n_A, n_B, and n'_A, n'_B are the concentration of two isotopically different components before and after processing.
- If required enrichment of gas A is attained in x-operation then,

$$(f_1)^x = \frac{n'_A / n'_B}{n_A / n_B}$$

$$= f \text{ or } x \log f_1 = \log\left[\frac{n'_A / n'_B}{n_A / n_B}\right]$$

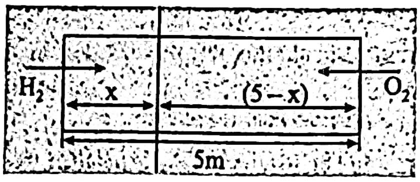
$$\text{or } x \log\left[\frac{M_B}{M_A}\right]^{1/2} = \log\left[\frac{n'_A / n'_B}{n_A / n_B}\right]$$

$$\text{or } \frac{x}{2}\log\left[\frac{M_B}{M_A}\right] = \log\left[\frac{n'_A / n'_B}{n_A / n_B}\right]$$

$$\boxed{\text{or } x = \frac{2\log\left[\frac{n'_A / n'_B}{n_A / n_B}\right]}{\log\left[\frac{M_B}{M_A}\right]}}$$

Train Your Brain

Example 8: In a tube of length 5 m, H_2 & O_2 are made to effuse into the tube from the identical opposite ends under identical conditions. Find the point where gases will meet for the first time.



Sol. $\frac{r_1}{r_2} = \frac{dx_1}{dt} \times \frac{dt}{dx_2} = \sqrt{\frac{M_2}{M_1}}$

$$\frac{dx_1}{dx_2} = \sqrt{\frac{32}{2}} = 4$$

$$\Rightarrow \frac{\text{distance travelled by } H_2}{\text{distance travelled by } O_2} = 4$$

$$\frac{x}{(5-x)} = 4$$

$x = (5 - x)\,4$; $x = 20 - 4x$; $5x = 20$; $x = 4$m from H_2 end

Example 9: Assume that you have a sample of hydrogen gas containing H_2, HD and D_2 that you want to separate into pure components (H = ^{1}H and D = ^{2}H). What are the relative rates of diffusion of the three molecules according to Graham's law?

Sol. $r_{H_2} : r_{HD} : r_{D_2} = \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}} = \sqrt{2} : \frac{2}{\sqrt{3}} : 1$

$= 1.41 : 1.15 : 1$

Concept Application

8. X mL of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical condition is:
   (*a*) 10 sec : He
   (*b*) 20 sec : O_2
   (*c*) 25 sec : CO
   (*d*) 55 sec : CO_2
9. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of n?
   (*a*) 1
   (*b*) 4
   (*c*) 3
   (*d*) 8
10. A gaseous mixture containing He, CH_4 and SO_2 was allowed to effuse through a fine hole then find out the molar ratio of gases coming out initially? (mixture contain He, CH_4 and SO_2 in 1 : 2 : 3 mole ratio).
   (*a*) 2 : 2 : 3
   (*b*) 6 : 6 : 1
   (*c*) $\sqrt{2} : \sqrt{2} : 3$
   (*d*) 4 : 4 : 3

KINETIC MOLECULAR THEORY OF GASES

The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory. Assumptions or postulates of the kinetic molecular theory of gases are given below. These postulates are related to atoms and molecule which cannot be seen, hence it is said to provide a microscopic model of gases.

- Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the **actual volume of the gas molecules is negligible in comparison to the empty space between them.** They are considered as point masses. This assumption explains the great compressibility of gases.

Credit:--- Divansh.....

- **There is no force of attraction between the particles of a gas at ordinary temperature and pressure.** The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. **Pressure is exerted by the gas as a result of collision of gas molecules the with the walls of the container.**
- **Collisions of gas molecules are perfectly elastic.** This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- **At any particular time, different particles in the gas have different speeds and hence different kinetic energies.** This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently, the particles must have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, **the molecular distribution of speeds remains constant at a particular temperature.**
- If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory, it is assumed that **average kinetic energy of the gas molecules is directly proportional to the absolute temperature.** It is seen that on heating a gas at constant volume, the pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently, thus, exerting more pressure.

  Kinetic theory of gases allows us to derive theoretically, all the gas laws studied in the previous sections. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.

Kinetic Gas Equation:

$$PV = \frac{1}{3}mNu^2$$

m = Total mass of the gas

N = Total number of molecules of the gas

u = root mean square velocity (U_{rms})

Application of Kinetic Gas Equation

For 1 mole N = N_0 (Avogadro number)

$m \times N_0$ = Molecular mass M.

(a) $PV = \frac{1}{3}Mu^2 \Rightarrow u^2 = \frac{3PV}{M} = \frac{3RT}{M}$

or $\boxed{(U_{rms}) = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}}$

(b) $PV = \frac{1}{3}Mu_{rms}^2 = \frac{2}{3} \times \frac{1}{2}Mu^2 = \frac{2}{3} \times \text{K.E./mole}$

or $\boxed{\frac{\text{K.E.}}{\text{mole}} = \frac{3}{2}RT}$

KINETIC ENERGY

- **Total translational kinetic energy**

$$\boxed{\frac{1}{2}mNu^2 = \frac{3}{2}PV = \frac{3}{2}nRT}$$

- **Average translational kinetic energy per molecule**

$$= \frac{3}{2}\frac{RT}{N_0} = \frac{3}{2}kT$$

Where $\left(k = \frac{R}{N_0}\right)$ is called Boltzmann's constant.

Its numerical value is 1.38×10^{-16} erg K^{-1} molecule^{-1}

Thus average K.E. is proportional to absolute temperature.

If T = 0 K (i.e., – 273.15°C), then average KE = 0

Thus, absolute zero (0 K) is the temperature at which molecular motion cases.

MOLECULAR SPEEDS

Molecules of gases remain in continuous motion. While moving they collide with each other and with the walls of the container. This results in change of their speed and redistribution of energy. So the speed and energy of all the molecules of the gas at any instant are not the same. Thus, we can obtain only average value of speed of molecules. If there are n number of molecules in a sample and their individual speeds are $u_1, u_2, \ldots\ldots u_n$, then average speed of molecules u_{av} can be calculated as follows:

$$u_{av} = \frac{u_1 + u_2 + \ldots. u_n}{n} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{2.55\frac{RT}{M}}$$

Where, R = universal gas constant

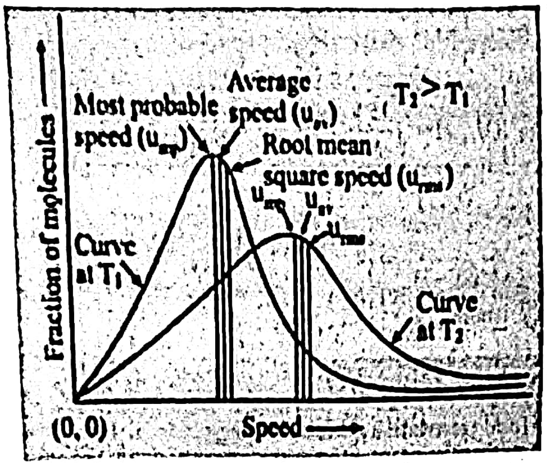
T = absolute temperature

M = Molar mass of the gas

Maxwell-Boltzmann Distribution of Molecular Speeds

Maxwell and Boltzmann have shown that actual distribution of molecular speeds depends on temperature and molecular mass of a gas. Maxwell derived a formula for calculating the number of molecules possessing a particular speed. Following graph shows schematic plot of number of molecules v/s. molecular speed at two different temperatures T_1 and T_2 (T_2 is higher than T_1). The distribution of speeds shown in the plot is called **Maxwell-Boltzmann distribution of speeds.**

Credit:--- Divansh.....



Maxwell-Boltzmann distribution of speeds

The graph shows that number of molecules possessing very high and very low speed is very small. **The maximum in the curve represents speed possessed by maximum number of molecules. This speed is called most probable speed, u_{mp}.**

$$u_{mp} = \sqrt{\frac{2RT}{M}}$$

This is very close to the average speed of the molecules. On increasing the temperature most probable speed increases. Though at a particular temperature the individual speed of molecules keeps changing, the distribution of speeds remains same. Also, **speed distribution curve broadens at higher temperature.** Broadening of the curve shows that number of molecules moving at higher speed increases. Speed distribution also depends upon mass of molecules. **At the same temperature, gas molecules with heavier mass have slower speed than lighter gas molecules.** For example, at the same temperature lighter nitrogen molecules move faster than heavier chlorine molecules. Hence, at any given temperature, nitrogen molecules have higher value of most probable speed than the chlorine molecules.

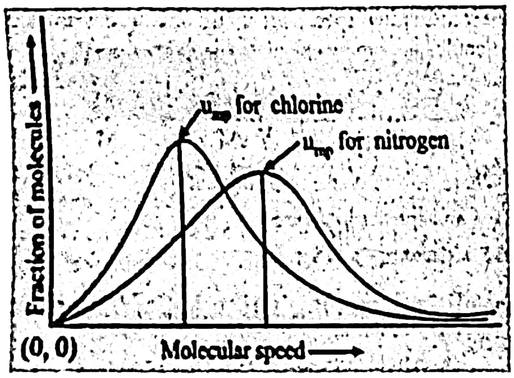


Fig. Distribution of molecular speeds for chlorine and nitrogen at 300 K

We know that kinetic energy of a particle is given by the expression:

$$\text{Kinetic Energy} = \frac{1}{2}mu^2$$

Therefore, if we want to know average translational kinetic energy, $\frac{1}{2}m\overline{u^2}$, for the movement of a gas particle in a straight line, we require the value of mean of square of speeds, $m\overline{u^2}$, of all molecules. This is represented as follows:

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + ...u_n^2}{n}$$

If we take the square root of the mean of the square of speeds then we get a value of speed which is different from most probable speed and average speed. This speed is called **root mean square speed** and is given by the expression as follows:

Root mean square speed is the direct measure of the average kinetic energy of gas molecules.

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3PV}{M}}$$

- Root mean square speed, average speed and the most probable speed have following relationship:

  $u_{rms} > u_{av} > u_{mp}$ (For given gas at given temperature)
- The ratio between the three speeds is given below:

  $u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224$

COLLISION FREQUENCY, COLLISION DIAMETER AND MEAN FREE PATH

The collision rate (i.e., the number of collisions taking place in unit time per unit volume) is called **collision frequency** (z) and is given by

$$z = \frac{\pi n^2 \sigma^2 u_{avg}}{\sqrt{2}}$$

The average of distances travelled by a molecule between successive collisions is called **mean free path** (λ).

$$\lambda = \frac{1}{\sqrt{2}\pi n\sigma^2}$$

where n is the number of molecules per unit molar volume.

u_{avg} = average velocity,

σ = **collision diameter i.e.,** the minimum distance between the centres of two molecules when at the point of collision.

Also based on kinetic theory of gases, mean free path $\lambda \propto \frac{T}{P}$.

Thus,

- Larger the size of the molecules, smaller the mean free path.
- Greater the number of molecules per unit volume, smaller the mean free path.
- Larger the temperature, larger the mean free path.
- Larger the pressure, smaller the mean free path.

Credit:--- Divansh.....

Train Your Brain

Example 10: Find the temperature at which methane and ethane will have the same rms speed respectively as carbon dioxide at 400°C.

Sol. $v_{rms}=\sqrt{\frac{3RT}{M}}$

$$\Rightarrow \frac{T_1}{M_1}=\frac{T_2}{M_2}$$

(*a*) $T_{CH_4}=\frac{673}{44}\times 16=244.73K$

(*b*) $T_{C_2H_6}=\frac{673}{44}\times 30=458.86K$

Example 11: Two gases A and B have the same value of most probable speed at 300 K for A and 150 K for B. Calculate the ratio of their molar masses.

Sol. Most Probable speed = $\left(\sqrt{\frac{2RT}{M}}\right)$

$$\frac{T_A}{M_A}=\frac{T_B}{M_B}$$

$$\therefore \frac{M_A}{M_B}=\frac{T_A}{T_B}=\frac{300}{150}\approx 2$$

$$\therefore M_A : M_B = 2 : 1$$

Example 12: Calculate the ratio of kinetic energy per mole of nitrogen at 27°C and hydrogen at 127°C.

Sol. Kinetic energy (K.E) = $\frac{168}{T}P$

$$KE_{N_2}=\frac{3}{2}RT_{N_2}$$

$$KE_{H_2}=\frac{3}{2}RT_{H_2}$$

$$\frac{KE_{N_2}}{KE_{H_2}}=\frac{T_{N_2}}{T_{H_2}}=\frac{300}{400}=\frac{3}{4}$$

Concept Application

11. The R.M.S. speed of the molecules of a gas of density 4 kg m^{-3} and pressure 1.2×10^5 N m^{-2} is:
    (*a*) 120 ms^{-1} (*b*) 300 ms^{-1}
    (*c*) 600 ms^{-1} (*d*) 900 ms^{-1}
12. The temperature of an ideal gas is increased from 120 K to 480 K. If at 120 K, the root-mean-square velocity of the gas molecules is v, at 480 K it becomes:
    (*a*) 4v (*b*) 2v
    (*c*) v/2 (*d*) v/4
13. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is
    (*a*) Two times that of a hydrogen molecules
    (*b*) Same as that of a hydrogen molecules
    (*c*) Four times that of a hydrogen molecules
    (*d*) Half that of a hydrogen molecules
14. Initially, the root mean square (rms) velocity of N_2 molecules at certain temperature is u. If this temperature is doubled and all the nitrogen molecules dissociate into nitrogen atoms, then the new rms velocity will be:
    (*a*) 2 u (*b*) 14 u
    (*c*) u / 2 (*d*) 4 u

REAL GASES (NON-IDEAL)

- Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.
- Real gases deviates from ideal behaviour because real gas molecules have a finite volume {since on liquefaction real gases occupy a finite volume}.
- Inter molecular attractive forces between real gas molecules is not zero {Real gases can be converted into liquid where as ideal gases can't be}.

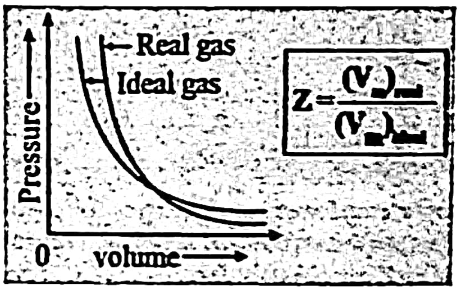
Compressibility Factor

- Deviation of real gases from ideal behaviour can be measured by using compressibility factor (Z).

$$Z=\frac{(PV)_{real}}{(PV)_{ideal}};\ (PV)_{ideal}=nRT$$

$Z=\frac{PV}{nRT}=\frac{PV_m}{RT}$, ($V_m$ is volume of one mole of gas or molar volume).

When $Z > 1$, $V_m > 22.4$ lit at STP ; When $Z < 1$, $V_m < 22.4$ lit at STP



Vander Waal Equation of Real Gases & Explanation of the Deviation from Ideal Gas Behaviour

The ideal gas equation does not consider the effect of attractive forces and molecular volume. Vander Waal corrected the ideal gas equation by considering

(*a*) Molecular volume (*b*) Molecular attraction

Credit:--- Divansh.....

- **Volume correction:**

Ideal gas equation:

$P_iV_i = nRT$; In the equation 'V_i' or V_{ideal} stands for the volume which is available for free movement of the molecules.

hence, $V_i = V -$ {volume not available for free movement}

For an ideal gas

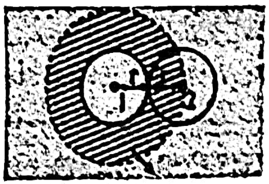
$V_i = V$ {V = volume of container}

but for a real gas

$V_i \neq V$, as all the volume is not available for free movement

Molecules have finite volume: The volume that is not available for free movement is called **excluded volume.**

let us see, how this excluded volume is calculated.



Excluded volume
(not available for free)

For above example, the entire shaded region is excluded, as it's centre of mass cannot enter this region.

If both molecules were ideal, then they would not have experienced any excluded volume but not in the case, of real gas as the centre of mass of '2' cannot go further.

Hence for this pair of real gas molecules,

$$\text{Excluded volume per molecule} = \frac{1}{2}\left\{\frac{4}{3}\pi(2r)^3\right\}$$

$$= 4\left\{\frac{4}{3}\pi r^3\right\}$$

⇒ **excluded volume per mole of gas molecule (b)**

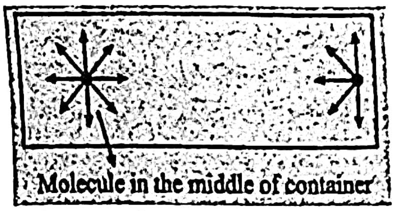
$$= N_A 4\left\{\frac{4}{3}\pi r^3\right\}$$

$= 4 \times N_A \times$ **Volume of individual molecule**

for n moles, excluded volume = nb

$V_i = V - nb$ = volume correction

- **Pressure correction or effect of molecular attraction forces:**



Due to attractive forces, speed during collisions will be reduced ⇒ Force applied on wall and hence momentum change will be less ⇒ Pressure will be less.

$P_{ideal} = P +$ {correction term}

Correction term $\propto$ no. of molecules attracting the colliding molecule $\propto (n/V)$.

Correction term $\propto$ density of molecules $\propto (n/V)$.

no. of collision $\propto$ density of molecules $\propto \left(\frac{n}{V}\right)$

$$\text{net correction term} \propto \left(\frac{n}{V}\right)\left(\frac{n}{V}\right) = \frac{an^2}{V^2}$$

'a' is constant of proportionality and this is dependent on force of attraction

Stronger the force of attraction, greater will be 'a' (Constant)

$$P_i = P + \frac{an^2}{V^2}$$

Vander Waal equation is $\boxed{\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT}$

Significance

- Easily liquefiable gases like SO_2, NH_3, H_2S, CO_2 have high values of "a" than the permanent gases like N_2, H_2, O_2 etc. "a" measures the intermolecular force of attractions acting between the molecules.

Key Note

- The value of 'a' depends on inter molecular attractive forces.
- The value of 'a' for polar molecule > 'a' valuc for non polar molecule.
- The value of 'b' $\propto$ size of gas molecules.

Limitations

(a) At very high pressure and very low temperature it is not valid due to the fact that the values of the Vander Waal constant "a" and "b" don't remain constant over the entire ranges of temperature and pressure.

(b) The values of "a" and "b" are found to vary with P and T.

(c) It couldn't explain the qualitative aspect of deviations so satisfactorily as it could explain the quantitative aspect of deviations.

Units of "a" and "b":

Unit of "a":

$$a = \frac{PV^2}{n^2} = \frac{atm \times lit^2}{mol^2} = lit^2 atm.mol^{-2}$$

Unit of "b":

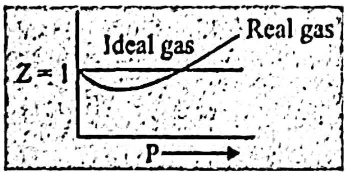
b = incompressible vol./mole.

$v - nb = 0, \qquad v = nb$

$$b = \frac{v}{n} = lit.mol^{-1}$$

VANDER WAAL'S EQUATIONS AT DIFFERENT CONDITIONS

Variation of Z with P for vander waals' equation at any temp.



Vander waal equation for 1mole:

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

- **At Low Pressure**

At low pressure, V_m will be high.

Hence b can be neglected in comparison to V_m but $\frac{a}{V_m^2}$ can't be neglected as pressure is low

Thus equation would be $\boxed{\left(P+\frac{a}{V_m^2}\right)V_m=RT}$

$$PV_m+\frac{a}{V_m}=RT$$

$$\frac{PV_m}{RT}+\frac{a}{V_mRT}=1$$

$$\boxed{Z=1-\frac{a}{V_mRT}} \Rightarrow Z<1$$

Real gas is easily compressible as compared to an ideal gas.

- **At High Pressure** (moderate temperature) V_m will be low so 'b' can't be neglected in comparison to V_m but $\frac{a}{V_m^2}$ can be neglected as compared to much higher values of P.

Then vander waal's equation will be

$$P(V_m-b)=RT$$

$$PV_m-Pb=RT$$

$$\frac{PV_m}{RT}=\frac{Pb}{RT}+1$$

$$Z=\frac{Pb}{RT}+1 \quad Z>1$$

If $Z>1$, then gas is more difficult to compress as compared to an ideal gas.

- **AT Low Pressure and Very High Temperature**

V_m will be very large hence 'b' can be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large

$PV_m = RT$ (ideal gas condition) i.e., $Z=1$

Exceptional Behaviour of Hydrogen and Helium

- Since both hydrogen and helium have comparatively small molar masses, the attractive forces between their molecules are too small, hence $a=0$.
- In other words, the correction term(a/V_m^2) due to the attraction factor remains negligible at ordinary temperatures. Thus

$$P(V_m-b)=RT$$

$PV_m = RT + Pb$ i.e., $Z>1$ at ordinary temperature

$$\text{So } Z=1+\frac{Pb}{RT}$$

Plots of Compressibility Factor vs Pressure:

(i) For an ideal gas $Z=1$ and is independent of temperature and pressure.

(ii) For the gases which are easily liquefied (e.g. CO_2), Z dips sharply below the ideal line in the low pressure region.

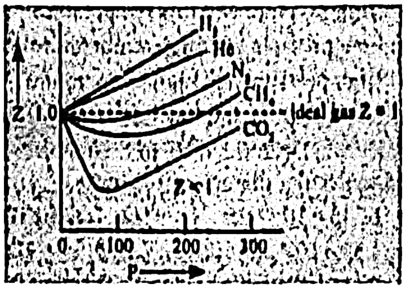


Fig. Variation of Z with pressure at constant temperature.

(iii) **Effect of temperature:** An increase in temperature shows a decrease in deviation from ideal behaviour i.e. PV_m approaches RT or Z approaches unity with increase in temperature.

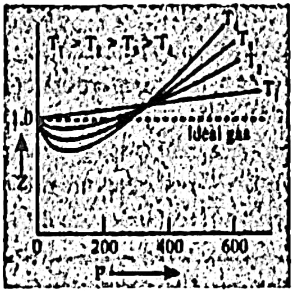


Fig. Variation of Z with pressure at different temperature.

Train Your Brain

Example 13: Arrange following in decreasing value of 'a' (H_2O, CO_2, Ar)

Sol. $H_2O > CO_2 > Ar$

For non polar molecules: Greater the size or surface area, greater will be vander waal's forces, so greater will be 'a'.

Example 14: Arrange following gases according to value of 'a' : He, Ar, Ne, Kr.

Sol. $a_{Kr} > a_{Ar} > a_{Ne} > a_{He}$

Example 15: Arrange the following according to liquification pressure: n-pentane ; iso-pentane, neo pentane.

Sol. $a_{n\text{-pentane}} > a_{iso\text{-pentane}} > a_{neo\text{-pentane}}$

liquification pressure = LP

$LP_{n\text{-pentane}} < LP_{iso\text{-pentane}} < LP_{neo\text{-pentane}}$

Example 16: Two vander waal's gases have same value of 'b' but different 'a' values. Which of these would occupy greater volume under identical conditions?

Sol. If two gases have same value of 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume. This is because the gas with a larger value of 'a' will have larger force of attraction and hence lesser distance between its molecules.

Credit:--- Divansh.....

Concept Application

15. A gas behaves like an ideal gas at:
    (*a*) High pressure and low temperature
    (*b*) Low pressure and high temperature
    (*c*) High pressure and high temperature
    (*d*) Low pressure and low temperature
16. Vander Waal's constant 'b' of helium is 24 mL mol^{-1}. Find molecular diameter of helium.
    (*a*) 1.335×10^{-10} cm (*b*) 1.335×10^{-8} cm
    (*c*) 2.67×10^{-8} cm (*d*) 4.34×10^{-8} cm
17. For a gas, deviation from ideal behaviour is maximum at:
    (*a*) 0°C and 1.0 atm (*b*) 100°C and 2.0 atm
    (*c*) –13°C and 1.0 atm (*d*) –13°C and 2.0 atm
18. Consider the equation $Z = \frac{PV}{RT}$. Which of the following statements is correct?
    (*a*) When Z>1, real gases are easier to compress than the ideal gas
    (*b*) When Z = 1, real gases get compressed easily
    (*c*) When Z > 1, real gases are difficult to compress
    (*d*) When Z = 1, real gases are difficult to compress

BOYLE'S TEMPERATURE (T_B)

The temperature at which a real gas behaves like an ideal gas over an appreciable range of pressure is known as Boyle's temperature (T_B). It means that at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e., Boyle's Law is obeyed. Mathematically we may express the Boyle temperature or Boyle point as the temperature where $\frac{\partial(PV)}{\partial P} = 0$ when $P \to 0$.

$$T_B = \frac{a}{Rb}$$

At Boyle's temperature the two effects, viz. finite size and the intermolecular attractions roughly compensate each other.

Above boyle temperature, the slope of Z versus P plot is positive; hence $b > \frac{a}{RT}$ or the size effect dominate the behaviour of the gas.

Below the boyle temperature the slope is negative; $b < \frac{a}{RT}$ or the intermolecular forces dominate the behaviour or the gas.

LIQUEFACTION OF GASES

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that exist in the liquid. A gas can be liquefied by:

(a) **Increasing pressure:** An increase in pressure results in an increase in attraction among molecules.

(b) **Decreasing temperature:** A decrease in temperature results in a decrease in kinetic energy of molecules.

Andrew's Isotherms:

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for CO_2. The types of isotherms are shown in figure.

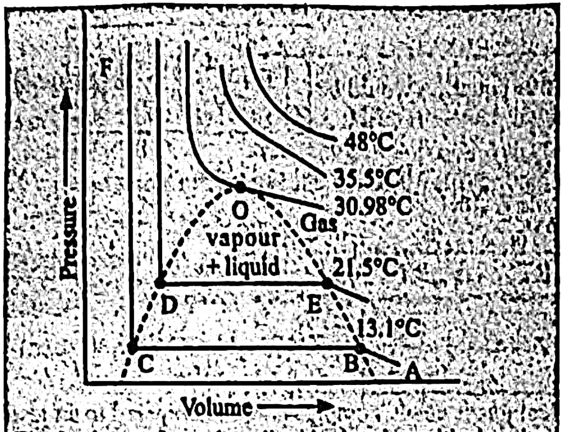


Fig. Isotherms for carbon dioxide showing critical region

Observations from Figure:

(a) **At low temperatures:** For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B).

At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density).

At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium.

CF represent liquid state.

The pressure corresponding to the line BC is there vapour pressure of the liquid.

(b) **At higher temperatures:** Similar type of curve as in case (a) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.

(c) **At high temperatures:** (like 48°C), the isotherms are like those of ideal gas.

(d) **At critical temperature (30.98°C):** The horizontal portion is reduced to a point. At point (O) CO_2, remains gas upto 73 atm pressure.

CRITICAL PARAMETERS

Critical temperature (T_C): The maximum temperature at which gas can be liquefied by the application of pressure alone i.e., the temperature above which a liquid cannot exist is called the critical temperature T_C.

- A gas below its critical temperature can be liquefied by applying pressure (P_C) and is called vapour of the substance.

Critical pressure (P_C): The minimum pressure required to liquefy the gas at the temperature T_C is called the critical pressure P_C.

Critical volume (V_C): The volume occupied by one mole of the gas at critical temperature, T_c and critical pressure, P_C is called the critical volume (V_C) of the gas.

- At critical temperature liquid phase passes into gaseous state imperceptibly and continuously.
- At critical temperature, density of vapour phase is equal to density of liquid phase.

The isotherm at T_C is called **critical isotherm**.

At point O, $\frac{dP}{dV} = 0$.

The point O is called the **point of inflection**.

Determination of Value of P_c, V_c and T_c:

(a) The Vander Waal equation is

$$\left(P+\frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\text{or } PV_m + \frac{a}{V_m} - Pb - \frac{ab}{V_m^2} = RT$$

$$\text{or } V_m + \frac{a}{p}\times\frac{1}{V_m} - b - \left(\frac{ab}{p}\right)\frac{1}{V_m^2} = \frac{RT}{P}$$

$$\text{or } V_m^3 + \frac{a}{P}V_m - bV_m^2 - \frac{ab}{P} = \frac{RTV_m^2}{P}$$

$$\text{or } V_m^3 - \left(b+\frac{RT}{P}\right)V_m^2 - \frac{a}{P}V_m - \frac{ab}{P} = 0 \quad \text{...(i)}$$

(b) This equation has three roots in V_m for given values of a, b, P and T. It is found that either all the three roots are real or one is real and the other two are imaginary.

(c) On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation V_m can be written as

$$(V_m - V')(V_m - V'')(V_m - V''') = 0$$

At the critical point $V' = V'' = V''' = V_C$

∴ the equation becomes,

$$(V_m - V_C)^3 = 0$$

$$\text{or } V_m^3 - V_C^3 - 3V_C V_m^2 + 3V_C^2 V_m = 0$$

from eq. (i)

$$V_m^3 - \left(b+\frac{RT}{P}\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0$$

(d) By comparing the coefficients

$$3V_C = b + \frac{RT_C}{P_C},\ 3V_C^2 = \frac{a}{P_C},\ V_C^3 = \frac{ab}{P_C}$$

(e) Therefore the value of critical compressibility factor in terms of Vander Waal constants is given by

$$\boxed{P_C = \frac{a}{27b^2};\ V_C = 3b;\ T_C = \frac{8a}{27Rb}}$$

⇒ At critical conditions, $Z = \frac{P_C V_{m,C}}{RT_C} = \frac{3}{8}$.

Key Note

- Boyle's temperature of a gas is always higher than its critical temperature (T_C).

Equation of Law of Corresponding State

All the equation defined for real gases involved gas dependent constant, hence if for two real gases n, P, V are same then the fourth parameter need not to be same and can be calculated only when the gas dependent constant is known. However instead of pressure, temperature, moles and volume, new reduced parameter are defined such that-

$$p_r = \frac{p}{p_c},\quad T_r = \frac{T}{T_c} \text{ and } V_r = \frac{V_m}{V_c}$$

$$p = p_r p_c,\quad T = T_r T_c \text{ and } V_m = V_r V_c$$

Substituting these expression in the van der Waals equation

$$\left(p+\frac{a}{V_m^2}\right)(V_m - b) = RT$$

We obtain $\left(p_r p_c + \frac{a}{V_r^2 V_c^2}\right)(V_r V_c - b) = RT_r T_c$

Replacing p_c, V_c and T_c in terms of a, b and R, we get

$$\left\{p_r \frac{a}{27b^2} + \frac{a}{V_r^2 (3b)^2}\right\}\{V_r(3b) - b\} = RT_r\left(\frac{8a}{27\,bR}\right)$$

i.e., $(p_r + (3/V_r^2))(3V_r - 1) = 8T_r$

From this equation the law of corresponding state can be stated **"two real gas having same no. of moles at same reduced temperature and same reduced volume have same reduced pressure".**

Behaviour of every gas is similar if it is at "identical" condition with respect to its critical condition

$$Z = \frac{pV_m}{RT} = \frac{(p_r p_c)(V_r V_c)}{R(T_r T_c)} = \frac{p_c V_c}{RT_c}\left(\frac{p_r V_r}{T_r}\right) = \frac{3}{8}\frac{p_r V_r}{T_r}$$

Virial Equation of State

It is a generalised equation of gaseous state.

Z is expressed in power series expansion of P or $\left(\frac{1}{V_m}\right)$

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \text{.....................}$$

B – second virial coefficient, C – third virial coefficient, D – fourth virial coefficient

Credit:--- Divansh.....

Vander waal equation in virial form:

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

$$P=\frac{RT}{(V_m-b)}-\frac{a}{V_m^2}$$

$$Z=\frac{PV_m}{RT}=\left[\frac{V_m}{(V_m-b)}\right]-\left[\frac{a}{V_m RT}\right]=\left[\frac{1}{(1-b/V_m)}\right]-\left[\frac{a}{V_m RT}\right]$$

$$\left[\text{As } \frac{1}{1-x}=1+x+x^2+x^3+\text{.........} \text{ for } |x|<1\right]$$

$$Z=\left(1+\frac{b}{V_m}+\frac{b^2}{V_m^2}+\frac{b^3}{V_m^3}+\text{...........}\right)-\frac{a}{V_m RT}$$

$$=1+\frac{1}{V_m}\left(b-\frac{a}{RT}\right)+\frac{b^2}{V_m^2}+\frac{b^3}{V_m^3}+\text{......}$$

comparing with virial equation

$$B=b-\frac{a}{RT},\ C=b^2,\ D=b^3$$

at low pressure : V_m will be larger hence $\frac{1}{V_m^2}, \frac{1}{V_m^3}$ can be neglected

$$Z=1+\frac{1}{V_m}\left(b-\frac{a}{RT}\right)$$

If $\left(b-\frac{a}{RT}\right)=0 \Rightarrow$ at $\boxed{T=\frac{a}{Rb}}$, $Z=1$ (ideal gas)

So at $T=\frac{a}{Rb}$; gas will behave as an ideal gas

But at constant temperature ideal gas equation obeys Boyle's law

at $T=\frac{a}{Rb}$, so the temp is called Boyle's temp.

Joule - Thomson Effect

- If a compressed gas is allowed to undergo free expansion, it may show cooling or heating or no change in temperature depending on the nature of the gas.
- In case of ideal gas there is no heating or cooling effect.
- In case of non ideal gas having negative deviation, if gas is allowed to expand adiabatically then the separating molecules have to do work against mutual attraction at the cost of their own K.E. So, temperature falls.

Inversion Temperature

The temperature below which a gas on subjecting to Joule Thomson effect shows cooling effect (μ_{JT} = +ve) and above which it shows heating effects (μ_{JT} = –ve) is called inversion temperature (T_i)

$$T_i=\frac{2a}{Rb}$$

μ_{JT} = Joule Thomson coefficient expressed as

$$\left(\frac{\delta T}{\delta P}\right)_H=\mu_{JT}$$

If $T > T_i$ heating is produced

If $T < T_i$ cooling is produced

If $T = T_i$ neither heating nor cooling

$$T_i=\frac{2a}{Rb}=2T_B$$

LIQUID STATE

In liquid state, molecules are farther apart in comparison to solids and closer in comparison to gases. Therefore, it is regarded as condensed gas or fused solid. But it is more similar to solids.

General Properties of liquids:

- Liquids has definite volume.
- Density of liquids is more than that of gases.
- Liquids do not have their own shape. They acquire the shape of the container in which they are filled.
- Diffusion of liquid is slow as compared to gases.
- Liquids are non-compresssible as compared to gases.
- Rate of vaporisation increases on increasing the surface area of a liquid.

Vapour Pressure

- When there is an equilibrium between vaporisation and condensation, then pressure exerted by the vapour on the surface of the liquid is called its vapour pressure.

Factors Affecting Vapour Pressure

(I) **Nature of Liquids:** Vapour pressure is lower when molecules of liquid have stronger attractive forces between them.

Vapour Pressure of Different Liquids at 20°C

More polar	H_2O	$2.33 \times 10^{-3}\ Nm^{-2}$
Less polar	C_2H_5OH	$5.790 \times 10^{-3}\ Nm^{-2}$
Nonpolar	CCl_4	$12.130 \times 10^{-3}\ Nm^{-2}$

(II) **Temperature:** Vapour pressure increases on increasing temperature. Comparison of vapour pressure of a liquid at different temperatures can be done by Clausius-Clapeyron Equation.

$$\log\frac{P_2}{P_1}=\frac{\Delta H_{Vap}}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Boiling Point

At constant pressure, the temperature at which vapour pressure of a liquid is equal to the atmospheric pressure, is called boiling point of the liquid.

- When external pressure is increased, then higher amount of heat is required. Due to this, boiling point increases. For example, food gets cooked faster in a pressure cooker due to increase in boiling point.
- Contrary to this, on reducing external pressure (as on the mountains), boiling point decreases. Due to this, food cooks slower on mountains.

Viscosity

Resistance of liquid towards its flow is called viscosity.

The liquids whose viscosity is high, are viscous and flow slowly. e.g., honey, glycerol, conc. H_2SO_4, etc. The liquids whose viscosity is low, flow faster. e.g. water, alcohol, ether, etc. Viscosity is due to internal frictional force of liquids.

Viscosity Coefficient, η

Force required per unit area for keeping unit difference in velocity of two parallel layers one cm apart in a liquid, is called viscosity coefficient.

$$f \propto A\left(\frac{dV}{dx}\right)$$

$$f = \eta A\left(\frac{dV}{dx}\right)$$

where f = Static force which is exerted in the direction of flow of liquid.

η = Viscosity coefficient

dx = Distance between two layers

dv = Difference in the velocity of two layers

A = Contact area

Value of η depends on the nature of the liquid at constant temperature. If A = 1 sq. cm, v = 1 cm/second and x = 1 cm, then f = η

CGS unit of η: Dyne second cm^{-2} = Poise

SI unit of η: $Nm^{-2} \times$ sec or Pascal sec.

> The property opposite of viscosity is called fluidity.
>
> $$f = \frac{1}{\eta}$$

Factors Affecting Viscosity

(i) **Intermolecular Forces:** Higher the attractive forces between the molecules of liquid, higher will be the viscosity. Due to hydrogen bonding, viscosity of water is high. Hydrogen bonds are of greater extent in glycerine, because there are three OH groups. Therefore, viscosity of glycerine is higher than that of water.

(ii) **Molecular Weight:** Attractive forces between molecules (Vander Waal force and hydrogen bonding) increase with increase in molecular weight. Therefore, viscosity increase.

(iii) **Shape of Molecules:** Viscosity of branched-chain compound is higher in comparison to unbranched-chain compounds.

(iv) **Pressure:** Viscosity increases with increase in pressure.

(v) **Temperature:** Strength of intermolecular attractive forces decrease on increase in temperature. Therefore, viscosity also decreases.

Viscosity in Everyday Life:

Lubricant is used on the basis of its viscosity. Blood is a viscous liquid. Blood circulation gets obstructed because amount of steroids, like cholesterol, increases in blood. Due to increase of pressure on heart, heart attack may occur.

Surface Tension

There are strong attractive forces between the molecules of a liquid. Molecules of the liquid are attracted equally from all the directions. Therefore, these forces cancel each other. But the molecules of the surface are attracted by the molecules below the surface only. Thus, surface of liquid feels tension and forms a tight membrane. This property is called surface tension.

The vertical force exerted per cm length at the surface of a liquid is called surface tension.

γ = Change in area/work

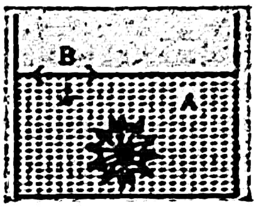


Fig. Surface tension in liquids.

Unit of surface tension in CGS system = Dyne per cm

SI unit – Newton per meter

Globular shape of liquid drop, rising and falling of liquid in capillary tube and convex surface of liquid, are all due to surface tension.

Factors Affecting Surface Tension

(i) **Temperature:**

Intermolecular attractive forces decrease on increasing temperature. Therefore, surface tension decreases.

(ii) **Nature of Solute:**

(a) Surface tension decreases on adding soap, detergent, etc. Due to this reason, oily substance gets removed from the surface of the cloth, and the substance present in toothpaste also reduces surface tension.

(b) Surface tension decreases when a liquid having low surface tension is added to it or its amount is increased.

(c) Surface tension goes on increasing when a liquid having high surface tension is added or its amount is increased.

Following phenomenon can be explained on the basis of surface tension.

- Globular shape of small droplets of liquid.
- Cleansing action of soaps and detergents.
- Movement of insects on the surface of water.
- Capillary action

Train Your Brain

Example 17: Which of the following statements are correct?

I. The magnitude of surface tension of a liquid depends on the attractive forces between the molecules.

II. Surface tension decreases with increase in temperature.

The correct option is

(*a*) Only I (*b*) Only II

(c) Both I and II (*d*) Neither I nor II

Sol. (*c*) The magnitude of the surface tension of a liquid depends on the attractive forces between the molecules. Surface tension decreases with increase in temperature. Both I and II statements are correct.

Example 18: Vapour pressure increases with increase in

(*a*) Concentration of solution containing non-volatile solute

(*b*) Temperature upto boiling point

(*c*) Temperature upto triple point

(*d*) Altitude of the concerned place of boiling

Sol. (*b*) Vapour pressure increases with increase in temperature up to boiling point. When vapour pressure of liquid equal to atmospherical pressure, liquid begins to boil.

Concept Application

19. When you look directly up at the sky, you are actually looking through a very tall, transparent column of air that extends from the surface of the earth thousands of kilometers into space. If the air in this column were liquefied, how tall would it be? The density of liquid air is 0.89 g ml^{-1}.

GAS EUDIOMETRY AND DETERMINATION OF MOLECULAR FORMULA OF GAS

In Eudiometry, we determine the composition of gaseous mixtures and molecular formula for gases and gaseous hydrocarbons.

The fundamental principle involved in gas eudiometry is the Avogadro's law: "*Volume of the gas is proportional to the number of moles of gas at constant temperature and pressure*".

The gaseous mixture to be analyzed is mixed with known excess amount of oxygen and sparked. The volume of different gases produced as a result of combustion is determined by passing them thorough solution of certain compounds where by some components of the gaseous mixture are absorbed.

In general, all elements on oxidation with O_2 forms oxide with element in highest oxidation state and the volume of gases before combustion and after combustion is noted. Now the reaction mixture is brought to room temperature where $H_2O(g)$ condenses to $H_2O(l)$ which leads to contraction in volume. This is called first contraction. The volumes of CO_2, other gaseous products and remaining O_2 are determined by absorbing them in suitable reagents.

The contraction in volume due to cooling corresponds to the volume of water vapour. Thus in general, after cooling, the contraction in volume is given as: $V = V_R - V_P$

Where V_R = volume of reactants

V_P = volume of products.

Now, with the help of this method and Gay Lussac's method of combining volume, molecular formula and composition of gaseous mixtures can be determined.

- If reaction mixture contains nitrogen, it is not oxidized by O_2 even in presence of electric spark. This implies that in eudiometry, nitrogen is considered inert towards oxidation.

- The various reagents required for absorbing different gases are

Gases	**Adsorbed by**
O_2:	alkaline pyrogallol
O_3:	turpentine oil
NO :	$FeSO_4$ solution
CO:	ammoniacal Cu_2Cl_2 solution
H_2O vapour :	conc. H_2SO_4, fused $CaCl_2$ (required when reaction mixture is not brought to room temperature)
Cl_2:	water or alkali solution
NH_3:	acid solution or $CuSO_4$ solution
CO_2 & SO_2:	alkali solution (NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$ or ethanolamine ($HOCH_2CH_2NH_2$) etc.
N_2:	heated Mg

Consider a mixture of ethane (C_2H_6) and ethene (C_2H_4) measuring 'a' ml which is subjected to electric spark along with excess of oxygen (b ml. say). On sparking, C_2H_4 and C_2H_6 both get combusted and form gaseous CO_2 and H_2O vapours. Let us assume that the volume of C_2H_4 in the mixture be '*x*' ml. The combustion reactions are shown as

$$\begin{array}{lcccc} & C_2H_4 + & 3O_2 \longrightarrow & 2CO_2 + & 2H_2O \\ \text{Volume reacted/produced} & x & 3x & 2x & 2x \end{array}$$

$$\begin{array}{lcccc} & C_2H_6 + & (7/2)O_2 \longrightarrow & 2CO_2 + & 3H_2O \\ \text{Volume reacted/produced} & (a-x) & (7/2)(a-x) & 2(a-x) & 3(a-x) \end{array}$$

After explosion, the reaction mixture is allowed to come at room conditions where water vapour condenses to liquid H_2O.

Volume before sparking = a + b

Volume after sparking

$$= b - 3x - \frac{7}{2}(a-x) + 2x + 2(a-x) = b - x - \frac{3}{2}(a-x)$$

$\Rightarrow$ First contraction in volume after sparking = Volume before sparking – Volume after sparking

$$= (a+b) - \left[b - x - \frac{3}{2}(a-x)\right]$$

$$= \left[a + x + \frac{3}{2}(a-x)\right] = \left[\frac{1}{2}(5a-x)\right]$$

If V ml be the volume noted in this overall first contraction.

$$\therefore V = \left[\frac{1}{2}(5a-x)\right]$$

Thus the % composition of mixture would be determined as

$$\% \text{ of } C_2H_6 = \frac{a-x}{a} \times 100$$

$$\text{and } \% \text{ of } C_2H_4 = \frac{x}{a} \times 100$$

Train Your Brain

Example 19: 16 mL of a hydrocarbon gas was exploded with excess of oxygen. On cooling, the volume of the resulting gaseous mixture was reduced by 48 mL. When KOH was added, there was a further decrease of 48 mL in the volume. Find the molecular formula of the compound.

Sol. Since water vapour condenses to practically zero volume of water, the decrease in volume on cooling is the volume of water vapour, CO_2 is absorbed by KOH and so volume of CO_2 is equal to 48 mL.

Thus, C_xH_y (say) + $O_2 \rightarrow CO_2 + H_2O$

16 mL   48 mL   48 mL

Or   16 moles   48 moles   48 moles

Since C and H are completely converted to CO_2 and H_2O respectively, applying POAC for C and H atoms we get respectively,

$x \times$ moles of C_xH_y = 1 × moles of CO_2

$16x = 48, \Rightarrow x = 3$

$y \times$ moles of C_xH_y = 2 × moles of H_2O

$16y = 2 \times 48 \Rightarrow y = 6.$

Hence, the formula of the hydrocarbon is C_3H_6.

Concept Application

20. 20 ml of gas (N_xH_y) was completely decomposed by passing electric spark through it in an eudiometer. Volume after sparking was 40 ml. This was mixed with 45 ml of $O_2(g)$ and exploded. The resulting mixture contracted to 40 ml. Molecular formula of N_xH_y is_____.

(*a*) NH_3 (*b*) N_2H_2

(*c*) N_2H_4 (*d*) N_3H_3

MISCELLANEOUS

Calculation of Pay Load

Pay load is defined as the maximum weight that can be lifted by a gas filled balloon.

For maximum weight that can be lifted, applying force balance

$$F_{buoyancy} = M_{balloon} \times g + M_{pay\ load} \times g$$

$$\Rightarrow \rho_{air} \cdot V.g. = \rho_{gas} \cdot V.g + Mg + mg.$$

mass of balloon = m

volume of balloon = v

density of air = ρ_{air}

density of gas inside the balloon = ρ_{gas}

M = Mass of payload

MINDFUL COOKING AND SHARING

- Prepare a meal with care and intention, paying attention to the colors, smells, and textures of the ingredients.
- Share the meal with someone in need or invite a friend over, cherishing the act of giving and connection.

Credit:--- Divansh.....

Aarambh (Solved Examples)

1. An open container of volume V contains air at temperature 27°C or 300 K. The container is heated to such a temperature so that amount of gas coming out is 2/3 of

   (a) amount of gas initially present in the container

   (b) amount of gas finally remaining in the container

   Find the temperature (in kelvin) to which the container should be heated.

Sol. (a) Here, P & V are constant, n & T are changing. Let, initially the amount of gas present be n & temp. is 27°C or 300 K. Finally amount of gas present in container

$= n - \frac{2}{3} = n\left(\frac{1}{3}\times n\right)$ & Final temp. be T

Then using $n_1T_1 = n_2T_2$, we have,

$n \times 300 = \frac{n}{3} \times T_2 \Rightarrow T_2 = 900\text{ K}$

i.e., final temp = 900 K

(b) Let there be x moles of gas remaining in the container and $\frac{2}{3}$ x has come out

$\therefore \left(x + \frac{2}{3}x\right) = n \Rightarrow \frac{5x}{3} = n \therefore x = \frac{3n}{5}$

$\therefore$ Using $n_1T_1 = n_2T_2 \Rightarrow n \times 300 = \frac{3n}{5} \times T_2$

$\therefore T_2 = 500\text{ K}$

Final temperature = 500 K

2. Find the lifting power of a 100 litre balloon filled with He at 730 mm Hg and 25°C (Density of air = 1.25 g/L)

Sol. Since, PV = nRT, $PV = \frac{W}{M}RT$

$\therefore W = \frac{PVM}{RT} = \frac{730}{760} \times \frac{100 \times 4}{0.082 \times 298}$ g

i.e., Wt. of He = 15.72 g

Wt. of air displaced = 100 × 1.25 g/L = 125 g

∴ Lifting power of the balloon = 125 g − 15.72 g = 109.28 g

3. Some spherical balloons each of volume 2 litre are to be filled with hydrogen gas at one atm & 27°C from a cylinder of volume 4 litres. The pressure of the H_2 gas inside the cylinder is 20 atm at 127°C. Find number of balloons which can be filled using this cylinder. Assume that temperature of the cylinder is 27°C.

Sol. No. of moles of gas taken initially (in cylinder) $= \frac{PV}{RT}$

$= \frac{20 \times 4}{R \times 400} = 2.44$

No. of moles of gas left in cylinder $= \frac{1 \times 4}{R \times 300} = 0.163$

No. of moles of gas to be filled in balloons

= 2.44 − 0.163 = 2.277

Let we have 'n' balloons that we can fill

No. of moles of gas that can be filled in 1 balloon

$= \frac{1 \times 2}{0.082 \times 300} = 0.081$

$\therefore 0.081 \times n = 2.277$

n = 28 balloons.

4. Four one litre flasks are separately filled with the gases O_2, F_2, CH_4 and CO_2 under the same conditions. The ratio of number of molecules in these gases is:

   (a) 2 : 2 : 4 : 3 (b) 1 : 1 : 1 : 1

   (c) 1 : 2 : 3 : 4 (d) 2 : 2 : 3 : 4

Sol. According to Avogadro's hypothesis.

All the flasks contains same no. of molecules

∴ Ratio of no. of molecules of O_2, F_2, CH_4 & CO_2

= 1 : 1 : 1 : 1

5. A sample of water gas has a composition by volume of 50% H_2, 45% CO and 5% CO_2. Calculate the volume in litres (at STP) of water gas on treatment with excess of steam will result in total 5 litre of H_2. The equation for the reaction is:

   $CO + H_2O \rightarrow CO_2 + H_2$

Sol. If x L CO is needed then

Volume of H_2 in water gas $= \left(\frac{x}{0.45} \times 50\%\right)$ L

$= \left(\frac{x}{0.45} \times \frac{1}{2}\right)$ L $= \frac{x}{0.9}$ L

But, from equation $CO + H_2O \rightarrow CO_2 + H_2$

& Gay-Lussac's law, we get, that the volume of H_2

Produced = volume of CO taken.

∴ Volume of H_2 due to reaction = x L

∴ Total volume of $H_2 = \left(\frac{x}{0.9} + x\right)$ L = 5 L

$\Rightarrow \frac{1.9x}{0.9} = 5$ L

$\therefore x = \frac{0.9 \times 5}{1.9} \Rightarrow 2.37$

∴ Volume of water gas

$= \frac{x}{0.45}$ L $= \frac{2.37}{0.45}$ L = 5.27 L

6. A mixture of NO_2 & CO having total volume of 100 ml contains 70 ml of NO_2 at 1 atm is left for some time and some NO_2 get dimerised to N_2O_4 such that final volume of the mixture become 80 ml at 1 atm. calculate the mole fraction of NO_2 in final equilibrium mixture

   (a) $\frac{3}{8}$ (b) $\frac{5}{8}$ (c) $\frac{7}{16}$ (d) $\frac{5}{16}$

Sol. Initial volume of NO_2 = 70 ml

Initial volume of CO = 100 − 70 = 30 ml

Final volume of mixture = 80 ml

Let the volume of NO_2 in final mixture be x

Let 'V' ml NO_2 be converted to N_2O_4

$2NO_2 \rightarrow N_2O_4$

$V \qquad V/2$

Hence final volume

= volume of CO + volume of NO_2 left + volume of N_2O_4 formed

$30 + 70 - V + (V/2) = 80$

$V = 40$ ml

Hence volume of NO_2 left = 70 − V = 30 ml

Now as volume ∝ moles

$\therefore$ mole fraction = volume fraction = $\frac{30}{80} = \frac{3}{8}$

7. 5 ml of H_2 gas diffuses out in 1 sec from a hole. Find the volume (in ml) of O_2 that will diffuse out from the same hole under identical conditions in 2 sec.

Sol. Rate of diffusion of $H_2 = \frac{5\ ml}{1\ sec} = 5$ ml/s $= r_{H_2}$ (say)

rate of diffusion $\propto \sqrt{\frac{1}{\text{molar mass}}}$

$\therefore r_{O_2} = r_{H_2} \times \frac{1}{4} = 5\ ml/s \times \frac{1}{4}$

Volume of O_2 diffused in 2 seconds $= \frac{5}{4} \times 2$ ml
$= 2.5$ ml

8. A vessel contains H_2 & O_2 in the molar ratio of 8 : 1 respectively. This mixture of gases is allowed to diffuse through a hole. Find molar ratio of H_2 & O_2 in the mixture coming out of the hole.

Sol. Here, $n_{H_2} : n_{O_2} = 8 : 1$ & $\frac{r_{H_2}}{r_{O_2}} = \frac{n_{H_2}}{n_{O_2}}\sqrt{\frac{M_{O_2}}{M_{H_2}}}$

$\Rightarrow \frac{r_{H_2}}{r_{O_2}} = \frac{8}{1}\sqrt{\frac{32}{2}} = \frac{32}{1}$

$\Rightarrow \frac{\text{(no. of moles of } H_2 \text{ coming out)}/\Delta t}{\text{(no. of moles of } O_2 \text{ coming out)}/\Delta t} = \frac{32}{1}$

Required composition of $H_2 : O_2$ coming out = 32 : 1

9. If two gases of molecular weights M_A and M_B are at temperatures T_A and T_B, so that $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases?

(a) Density (b) Pressure

(c) KE per mol (d) RMS speed

Sol. Given that $T_A M_B = T_B M_A \Rightarrow \frac{T_A}{M_A} = \frac{T_B}{M_B}$

But r.m.s $= \sqrt{\frac{3RT}{M}}$

$\therefore r.m.s_A = \sqrt{\frac{3RT_A}{M_A}}$ & $r.m.s_B = \sqrt{\frac{3RT_B}{M_B}}$

$\therefore r.m.s_A = r.m.s_B$

10. Under critical states of a gas (for one mole), compressibility factor is

(a) $\frac{3}{8}$ (b) $\frac{8}{3}$ (c) 1 (d) $\frac{1}{4}$

Sol. For 1 mole of gas, $Z = \frac{P_c V_c}{RT_c}$ (Under critical condition)

But, $P_c = \frac{a}{27b^2}$, $V_c = 3b$, $T_c = \frac{8a}{27Rb}$

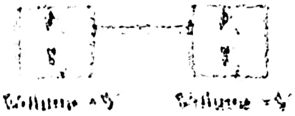
$$Z = \left(\frac{a}{27b^2}\right) \times \frac{3b}{R} \times \frac{27Rb}{8a} = \frac{3}{8}$$

11. Two closed vessel A and B of equal volume both containing air at pressure P_1 and temperature T_1 are connected to each other through a narrow open tube. If the temperature of one is now maintained at T_1 and other at T_2 (where $T_1 > T_2$) then what will be the final pressure?

(a) $P_f = \frac{2P_1T_2}{T_1 + T_2}$ (b) $P_f = \frac{2P_1T_1}{T_1 + T_2}$

(c) $P_f = \frac{T_1 + T_2}{2P_1T_2}$ (d) $P_f = \frac{T_1 + T_2}{4P_1T_1}$

Sol.



Initial total moles $= \frac{P_1V}{RT_1} + \frac{P_1V}{RT_1} = \frac{2P_1V}{RT_1}$

Final condition

P_f
T_1
P_f
T_2
V
V

Initial moles = final moles

$\frac{2P_1V}{RT_1} = \frac{P_fV}{RT_1} + \frac{P_fV}{RT_2}$

$\frac{2P_1}{T_1} = P_f\left(\frac{T_1 + T_2}{T_1T_2}\right)$

$\boxed{P_f = \frac{2P_1T_2}{T_1 + T_2}}$

12. One litre of a gaseous mixture of two gases effuses in 311 seconds while 2 litres of oxygen takes 20 minutes. The vapour density of gaseous mixture containing CH_4 and H_2 is:

Sol. Rate $= \frac{\text{Volume diffused}}{\text{time taken}}$

$r_1 = \frac{1}{311} \Rightarrow$ rate of mixture

Credit:--- Divansh.....

$$r_2 = \frac{2}{20\times60} \Rightarrow \text{rate of oxygen}$$

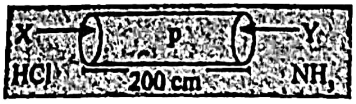
$$\frac{r_1}{r_2} = \sqrt{\frac{32}{\text{molar mass}}} = \frac{\frac{1}{311}}{\frac{2}{20\times60}}$$

$$\Rightarrow \sqrt{\frac{32}{\text{molar mass}}} = \frac{600}{311}$$

Molar mass of mixture = 8.6

$$\text{vapour density} = \frac{\text{molar mass}}{2} = \frac{8.6}{2} = 4.3$$

13. A straight glass tube as shown, has 2 inlets X & Y at the two ends of 200 cm long tube. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter in the tube at the same time and under the identical conditions. At a point P inside the tube, both the gases meet first. The distance (in cm) of point P from X is:



Sol. $\frac{r_{HCl}}{r_{NH_3}} = \sqrt{\frac{17}{36.5}}$

Let both the gases meet in time t

$\sqrt{17}t + \sqrt{36.5}t = 200$

$$t = \frac{200}{\sqrt{17}+\sqrt{36.5}}$$

$$= \frac{200}{4.12+6.04}$$

$$= \frac{200}{10.16}$$

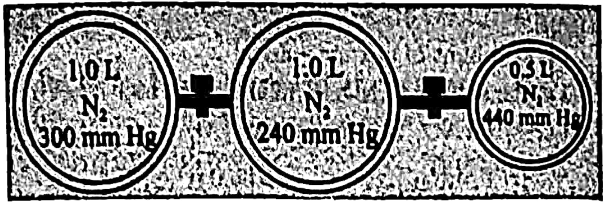
= 19.68 sec

Distance from x will be

$= 19.68 \times \sqrt{17}$

= 81.1 cm

14. Consider the arrangement of bulbs shown below.



If the pressure of the system when all the stopcocks are opened is x (in atm) then find value of 100 x.

(760 mm Hg = 1 atm)

Sol. Initial mole = final mole

$$\frac{300\times1}{RT} + \frac{240\times1}{RT} + \frac{440\times0.5}{RT} = \frac{P\times2.5}{RT}$$

$760 = P \times 2.5$

$$P = \frac{760}{2.5}\text{mm Hg}$$

$$P = \frac{2}{5}\text{atm} = x$$

$$100x = 100\times\frac{2}{5} = 40\text{atm}$$

15. A closed container of volume 30 litre contains a mixture of dinitrogen and dioxygen gases, at a temperature of 27°C and pressure of 4 atm. The total mass of the mixture is 148 gm. The moles of individual gases in the container are (Take R = 0.08 litre atm/mole.K)

Sol. $[n_{N_2} = 3, n_{O_2} = 2]$

$V = 30L$

$T = 300K$

$P = 4atm$

$PV = nRT$

$4 \times 30 = n \times 0.08 \times 300$

n = 5 moles

Let moles of $N_2 = n_1$

moles of $O_2 = 5 - n_1 = n_2$

$28n_1 + 32(5 - n_1) = 148$

$160 - 4n_1 = 148$

$4n_1 = 12$

$n_1 = 3$ & $n_2 = 2$

Credit:--- Divansh.....

IDEAL GAS EQUATION, GAS LAWS

1. If P, V, T represent pressure, volume and temperature of the gas, the correct representation of Boyle's law is

(*a*) $V \propto \frac{1}{T}$ (at constant P)

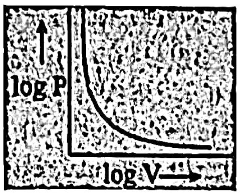
(*b*) $PV = RT$

(*c*) $V \propto 1/P$ (at constant T)

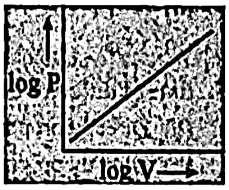
(*d*) $PV = nRT$

2. Which of the following represent log P vs log V variation as per Boyle's law?

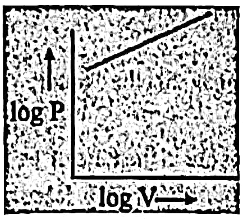
(*a*)



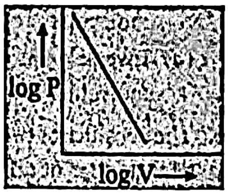
(*b*)



(*c*)



(*d*)



3. If 20 cm^3 gas at 1 atm is expanded to 50 cm^3 at constant T, then what is the final pressure (in atm) of gas?

(*a*) $20 \times \frac{1}{50}$ (*b*) $50 \times \frac{1}{20}$

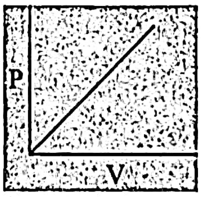
(*c*) $1 \times \frac{1}{20} \times 50$ (*d*) None of these

4. At the definite temperature, the volume of a definite mass of gas is 10 L at 5 atm pressure. At the same temperature, if the pressure of the gas is decreased to 1 atm, the volume of same gas becomes:

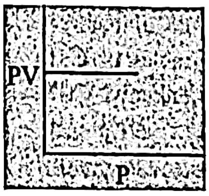
(*a*) 50 L (*b*) 2 L (*c*) 5 L (*d*) 0.5 L

5. Which of the following graphs represent Boyle's law?

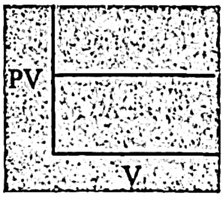
(*a*)



(*b*)



(*c*)



(*d*) (*b*) & (*c*) both

6. Which of the following expression at constant pressure represents Charles's law?

(*a*) $V \propto \frac{1}{T}$ (*b*) $V \propto \frac{1}{T^2}$

(*c*) $V \propto T$ (*d*) $V \propto d$

7. If two moles of an ideal gas at 546K occupy a volume of 44.8 litres, the pressure must be

(*a*) 2 atm (*b*) 3 atm

(*c*) 4 atm (*d*) 1 atm

8. Correct gas equation is

(*a*) $\frac{V_1T_2}{P_1} = \frac{V_2T_1}{P_2}$ (*b*) $\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$

(*c*) $\frac{P_1T_1}{V_1} = \frac{P_2V_2}{T_2}$ (*d*) $\frac{V_1V_2}{T_1T_2} = P_1P_2$

9. At constant temperature, if pressure of one mole of an ideal gas is increased by 25%, the volume of the gas.

(*a*) Increases by 25%

(*b*) decreases by 20%

(*c*) decreases by 25%

(*d*) Increases by 20%

10. A pre-weighed vessel was filled with oxygen at S.T.P. and weighed. It was then evacuated, filled with SO_2 at the same temperature and pressure, and again weighed. The weight of oxygen will be

(*a*) The same as that of SO_2

(*b*) Half of that of SO_2

(*c*) Twice that of SO_2

(*d*) One fourth that of SO_2

11. In the gas equation PV = nRT, the value of universal gas constant would depend only on

(*a*) The nature of the gas

(*b*) The pressure of the gas

(*c*) The temperature of the gas

(*d*) The units of measurement

12. When the pressure of 5L of N_2 is doubled and its temperature is raised from 300K to 600K, the final volume of the gas would be-

(*a*) 10 L (*b*) 5 L

(*c*) 15 L (*d*) 20 L

13. One litre of a gas collected at STP when kept at 2 atmospheric pressure and 27°C will occupy

(*a*) $\frac{300}{2 \times 273}$ litre (*b*) $\frac{2 \times 300}{273}$ litre

(*c*) $\frac{273}{2 \times 300}$ litre (*d*) $\frac{2 \times 273}{300}$ litre

Credit:--- Divansh.....

14. 273 mL of a gas at STP was taken to 27°C and 600 mm Hg pressure. The final volume of the gas would be

(*a*) 273 ml (*b*) 300 ml

(*c*) 380 ml (*d*) 586 ml

15. 10 g of hydrofluoric acid occupy 5.6 litre volume at STP. The empirical formula of the gas is HF. The molecular formula of the gas will be (At. mass of fluorine = 19)

(*a*) H_4F_4 (*b*) HF

(*c*) H_3F_3 (*d*) H_2F_2

16. A fire extinguisher contains 4.4 kg of CO_2. The volume of CO_2 delivered by this fire extinguisher at room temperature and 1 atm is

(*a*) 24.5 litre (*b*) 100 × 24.5 litre

(*c*) 10 × 24.5 litre (*d*) 1000 × 24.5 litre

17. The density of a gas at 27°C and 1 atm is d. Pressure remaining constant, at which of the following temperatures will its density become 0.75 d?

(*a*) 20°C (*b*) 30°C

(*c*) 400 K (*d*) 300 K

18. Two sealed containers of same capacity at the same temperature are filled with 44 g of hydrogen gas in one and 44 g of CO_2 in the other. If the pressure of CO_2 is 1 atm, what is the pressure in the hydrogen container?

(*a*) 1 atm (*b*) 0 atm

(*c*) 22 atm (*d*) 44 atm

19. If a mixture containing 3 moles of hydrogen and 1 mole of nitrogen is converted completely into ammonia, the ratio of initial and final volume under the same temperature and pressure would be:

(*a*) 3 : 1 (*b*) 1 : 3

(*c*) 2 : 1 (*d*) 1 : 2

20. The density of a gas A is three times that of a gas B at same temperature. If the molecular mass of A is M, the molecular mass of B is

(*a*) 3M (*b*) $\sqrt{3}$M

(*c*) M/3 (*d*) M$\sqrt{3}$

DALTON'S LAW OF PARTIAL PRESSURES

21. Dalton's law of partial pressures are applicable to mixture of

(*a*) Non reacting gases

(*b*) Ideal gases

(*c*) Both of these

(*d*) None of these

22. 1000 ml of a gas A at 600 torr and 500 ml of gas B at 800 torr are placed in a 2L flask. The final pressure will be

(*a*) 2000 torr (*b*) 1000 torr

(*c*) 500 torr (*d*) 1400 torr

23. If three unreactive gases having partial pressures P_A, P_B and P_C and their moles are 1, 2 and 3 respectively, then their total pressure will be

(*a*) $P = P_A + P_B + P_C$ (*b*) $P = \dfrac{P_A + P_B + P_C}{6}$

(*c*) $P = \dfrac{\sqrt{P_A + P_B + P_C}}{3}$ (*d*) None of these

GRAHAM'S LAW OF DIFFUSION

24. A certain gas effuses out of two different vessels A and B. A has a circular orifice while B has a square orifice of length equal to the radius of the orifice of vessel A. The ratio of rate of diffusion of the gas from vessel A to that from vessel B is

(*a*) $\pi : 1$ (*b*) $1 : \pi$

(*c*) 1 : 1 (*d*) 3 : 2

25. Rate of diffusion of a gas is

(*a*) Directly proportional to its density

(*b*) Directly proportional to its molecular mass

(*c*) Directly proportional to the square root of its molecular mass

(*d*) Inversely proportional to the square root of its molecular mass

26. The densities of two gases are in the ratio of 1 : 16. The ratio of their rates of diffusion is

(*a*) 16 : 1 (*b*) 4 : 1

(*c*) 1 : 4 (*d*) 1 : 16

27. A bottle of ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be

(*a*) At the centre of the tube

(*b*) Near the hydrogen chloride bottle

(*c*) Near the ammonia bottle

(*d*) Throughout the length of the tube

28. In an effusion experiment, it required 40 s for a certain number of moles of a gas of unknown molar mass to pass through a small orifice into a vacuum. Under the same conditions, 16 s were required for the same number of moles of O_2 to effuse. What is the molar mass of the unknown gas?

(*a*) 5.1 g/mol (*b*) 12.8 g/mol

(*c*) 80 g/mol (*d*) 200 g/mol

29. 50 ml of a gas A diffuse through a membrane in the same time as for the diffusion of 40 ml of gas B under identical conditions of pressure and temperature. If the molecular mass of A is 64, molar mass (in g/mol) of B would be

(*a*) 100 (*b*) 250

(*c*) 200 (*d*) 80

KINETIC THEORY OF GASES

30. Internal energy and pressure of a gas per unit volume are related as

(*a*) $P = \frac{2}{3}E$ (*b*) $P = \frac{3}{2}E$

(*c*) $P = \frac{1}{2}E$ (*d*) $P = 2E$

31. In deriving the kinetic gas equation, use is made of the root mean square velocity of the molecules because it is

(*a*) The average velocity of the molecules

(*b*) The most probable velocity of the molecules

(*c*) The square root of the average square velocity of the molecules

(*d*) The most accurate form in which velocity can be used in these calculations

32. The ratio of root mean square velocity to average velocity of gas molecules at a particular temperature is:

(*a*) 1.086 : 1 (*b*) 1 : 1.086

(*c*) 2 : 1.086 (*d*) 1.086 : 2

33. The ratio among most probable velocity, mean velocity and root mean square velocity is given by

(*a*) 1 : 2 : 3 (*b*) $1 : \sqrt{2} : \sqrt{3}$

(*c*) $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$ (*d*) $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$

34. Two vessel A and B in volume ratio 2 : 1 maintained at temperature 300 K and 600 K contain equal mass of CH_4 and O_2 respectively. The ratio of total translational kinetic energy of gas in flask A to that of flask B is:

(*a*) 1 : 1 (*b*) 2 : 1

(*c*) 4 : 1 (*d*) 1 : 4

35. Molecular velocities of the two gases at the same temperature are u_1 and u_2. Their molecular masses are m_1 and m_2 respectively. Which of the following expressions is correct?

(*a*) $\frac{m_1}{u_1^2} = \frac{m_2}{u_2^2}$ (*b*) $m_1u_1 = m_2u_2$

(*c*) $\frac{m_1}{u_1} = \frac{m_2}{u_2}$ (*d*) $m_1u_1^2 = m_2u_2^2$

36. If an ideal gas is allowed to expand at constant temperature, then

(*a*) Number of molecules of the gas decreases

(*b*) The kinetic energy of the gas molecules decreases

(*c*) The kinetic energy of the gas molecules increases

(*d*) The kinetic energy of the gas molecules remains the same

37. U_{rms} speed of O_2 at $\pi \times 10$ bar pressure in a 8 litre container containing 2 moles is:

(*a*) 10^3 cm/sec (*b*) $\sqrt{10^3}$ m/sec

(*c*) 10^3 m/sec (*d*) $\sqrt{2 \times 10^6}$ m/sec

38. In a closed flask of 5 litre, 1.0 g of H_2 is heated from 300 K to 600 K. Which statement is not correct?

(*a*) The rate of collision increases

(*b*) The energy of gaseous molecules increases

(*c*) The number of mole of the gas increases

(*d*) Pressure of the gas increases

39. The molecules of which of the following gas have highest speed?

(*a*) Hydrogen at –50°C (*b*) Methane at 298K

(*c*) Nitrogen at 1000°C (*d*) Oxygen at 0°C

REAL GAS

Vander Waal Equation and critical constants

40. Which of the following satisfies the greater compressibility of real gas?

(*a*) $Z < 1$

(*b*) At the higher pressure

(*c*) Above the Boyle's temperature

(*d*) Lesser the value of "a" but higher value of "b"

41. Gases deviate from the ideal gas behaviour because their molecules

(*a*) Possess negligible volume

(*b*) Have forces of attraction between them

(*c*) Are polyatomic

(*d*) Are not attracted to one another

42. The compressibility factor of a gas is defined as $Z = PV/RT$. The compressibility factor of an ideal gas is

(*a*) 0 (*b*) Infinity (*c*) 1 (*d*) –1

43. Vander Waal's equation of state is obeyed by real gases. For *n* moles of a real gas, the expression will be

(*a*) $\left(\frac{P}{n} + \frac{na}{V^2}\right)\left(\frac{V}{n-b}\right) = RT$

(*b*) $\left(P + \frac{a}{V^2}\right)(V - b) = nRT$

(*c*) $\left(P + \frac{na}{V^2}\right)(nV - b) = nRT$

(*d*) $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$

44. Which corresponds to greater deviation in the behaviour of a gas from the ideal gas equation PV = nRT?

(*a*) At high temperature and low pressure

(*b*) At low temperature and high pressure

(*c*) At high temperature and high pressure

(*d*) At low temperature and low high pressure

45. The Vander Waal's constant 'a' for the gases O_2, N_2, NH_3 and CH_4 are 1.3, 1.390, 4.170 and 2.253 L^2 atm mol^{-2} respectively. The gas which can be most easily liquefied is

(*a*) O_2 (*b*) N_2

(*c*) NH_3 (*d*) CH_4

Credit:--- Divansh.....

46. The compressibility factor of a gas is less than 1 at STP. Its molar volume V_m will be

(a) $V_m > 22.4L$

(b) $V_m < 22.4L$

(c) $V_m = 22.4L$

(d) None of these

47. The critical temperature of a gas is that temperature

(a) Above which it can no longer remain in the gaseous state.

(b) Above which it cannot be liquefied by pressure.

(c) At which it solidifies.

(d) At which the volume of the gas becomes zero.

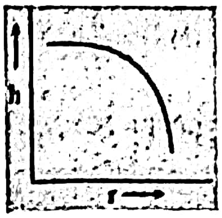
48. In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular force is

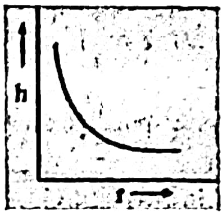
(a) $\left(P+\frac{a}{V^2}\right)$ (b) $(V-b)$

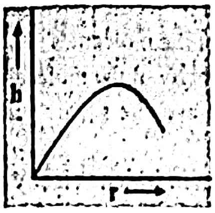
(c) RT (d) $\frac{1}{RT}$

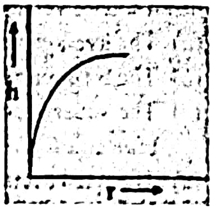
LIQUID STATE

49. Which of the following correctly represents the relation between capillary rise h and capillary radius r?

(a)


(b)


(c)


(d)


50. Surface tension does not vary with

(a) Temperature (b) Vapour pressure

(c) The size of surface (d) Concentration

51. Which among of the following has least surface tension?

(a) Benzene (b) Acetic acid

(c) Diethyl ether (d) Chlorobenzene

Parikshit (JEE Advanced Level)

SINGLE CORRECT TYPE QUESTIONS

1. For two gases, A and B with molecular weights M_A and M_B, it is observed that at a certain temperature T, the mean velocity of A is equal to the V_{rms} of B. Thus the mean velocity of A can be made equal to the mean velocity of B, if

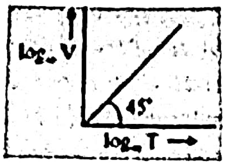
(a) A is at temperature T_1 and B at T_2 such that $T_1 > T_2$.

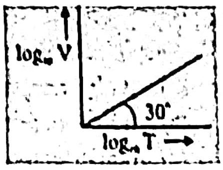
(b) Temperature of A is lowered to T_2 while B is at T_1 such that $T_2 < T_1$.

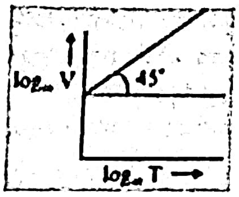
(c) Both A and B are raised to a higher temperature.

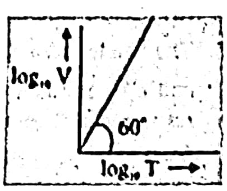
(d) Heat energy is supplied to A.

2. 10 mole of an ideal gas are confined in a cylinder fitted with frictionless, weight less piston. If constant pressure of 0.821 atm is maintained by piston and cylinder is heated slowly to raise the volume, then which graph correctly represents the behaviour of gas?

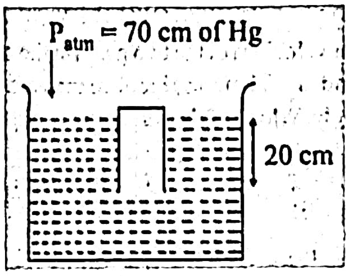
(a)


(b)


(c)


(d)


3. A tube closed at one end is dipped in mercury as shown in figure such that the closed surface coincides with the mercury level in the container. By how much length of the tube should be extended such that the level of Hg in the tube is 5 cm below the mercury level inside the container? (Assume temperature remains constant)



(a) 18 cm (b) 19 cm (c) 24 cm (d) 30 cm

4. A sample of UF_6 contains $^{235}UF_6$ and $^{238}UF_6$ in the ratio of 0.7 : 100. How many times should the effusion process be carried out to enrich ^{235}U to the extent of 7.0%?

(a) 218 (b) 420 (c) 538 (d) 518

5. In Neptune, we can have a Celsius type of scale (called the Neptune scale) of temperature, based on the melting point 0°N and the boiling point 100°N of hydrogen. In the limit of zero pressure, PV = 28 lit. atm at 0°N and 40 lit. atm at 100°N. What is the value of 0°A on the Neptune scale of temperature?

(a) −118.2°N (b) −152.5°N

(c) −283.1°N (d) −233.3°N

Credit:--- Divansh.....

6. My weight is 80 kg. I want to fly in the sky with the aid of balloons each containing 50 moles of H_2 gas at 0.05 atm pressure and 27°C temperature. If the density of air at the given condition is 1.25 gm lit, how many such type of balloons do I need to attach with myself to fly in the sky?

(*a*) 3
(*b*) 6
(*c*) 1
(*d*) 8

7. For a real gas (van der Waals gas) behaving ideally (at Boyle's temperature), the pressure may be

(*a*) $a.b.V_m$
(*b*) $\frac{V_m}{a.b}$
(*c*) $\frac{a}{V_m.b}$
(*d*) $\frac{b}{V_m.a}$

8. Under identical conditions of pressure and temperature, 4L of gaseous mixture (H_2 and CH_4) effuses through a hole in 5 min whereas 4 L of a gas X of molecular mass 36 takes 10 min to effuse through the same hole. The mole ratio of $H_2 : CH_4$ in the mixture is

(*a*) 1 : 2 (*b*) 2 : 1 (*c*) 2 : 3 (*d*) 1 : 1

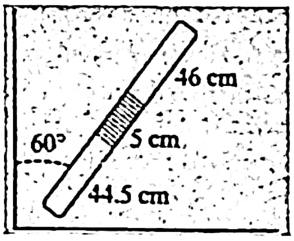
9. There are 2n containers having volume V, 2V, 3V ...... 2nV. A fixed mass of a gas is filled in all containers connected with stopcock. All containers are at the same temperature. If pressure of first container is P then final pressure, when all stopcocks are opened is:

(*a*) $\frac{P}{(2n+1)}$
(*b*) $\frac{P}{(n+1)}$
(*c*) $\frac{2P}{(n+1)}$
(*d*) $\frac{2P}{(2n+1)}$

10. The pressure of a gas inside a spherical container is maintained at 2 atm. If the average velocity of the gas molecules inside the container is increased by a factor of two, keeping the pressure same, then by what factor would surface area of container increase?

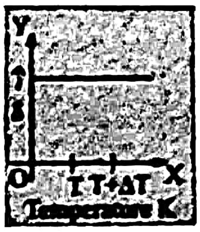
(*a*) $2^{2/3}$
(*b*) $2^{4/3}$
(*c*) $2^{-1/3}$
(*d*) 1

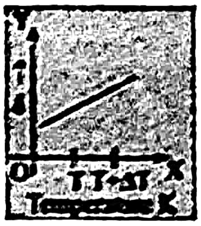
11. A thin tube of uniform cross section has trapped air columns of lengths 46 and 44.5 cm above and below a middle pellet of mercury 5 cm in length (see figure) when held at an angle of 60° to the vertical. When placed horizontally, the columns are equal in length. The temperature is 27°C. The pressure of air columns, in cm Hg, when the tube is horizontal, is

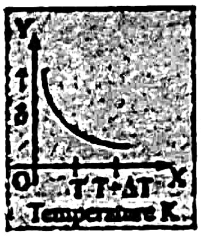


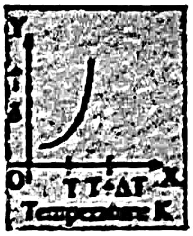
(*a*) 76.0 cm
(*b*) 71.7 cm
(*c*) 73.2 cm
(*d*) 75.4 cm

12. An ideal gas is initially at temperature T and volume V. Its volume increases by ΔV due to an increase in temperature of ΔT, pressure remaining constant. The quantity $\delta = \frac{\Delta V}{V\Delta T}$ varies with temperature as

(*a*)


(*b*)


(*c*)


(*d*)


13. The correct equation for Boyle's law is

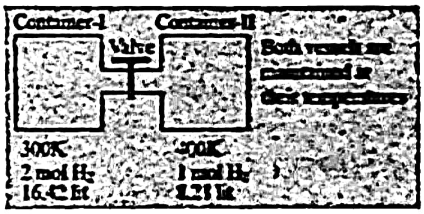
(*a*) $\frac{d^2P}{P} = -\frac{dV}{dT}$
(*b*) $\frac{d^2P}{P} = +\frac{d^2V}{dT}$
(*c*) $\frac{dP}{P} = -\frac{dV}{V}$
(*d*) $\frac{dP}{P} = +\frac{dV}{V}$

MULTIPLE CORRECT TYPE QUESTIONS

14. Select the correct observation for a 8.21L container, filled with 2 moles of He at 300 K.

(*a*) It has pressure 6 atm.
(*b*) If it is an open rigid container, its pressure increases to 8 atm on heating to 400 K.
(*c*) If it is closed non-rigid (like thin skin balloon), its volume increases to 16.42 litre on heating to 600 K.
(*d*) When connected with another similar empty container maintained at 150 K while maintaining original container at 300 K, pressure reduces to $\frac{2}{3}$ atm.

15. Select the correct option(s) :



(*a*) Pressure in container-I is 3 atm before opening the valve.
(*b*) Pressure after opening the valve is 3 atm.
(*c*) Moles in each compartment are same after opening the valve.
(*d*) Pressure in each compartment are same after opening the valve.

Credit:--- Divansh.....

16. The rate of diffusion of two gases 'A' and 'B' are in the ratio of 16 : 3. If the ratio of their masses present in the mixture is 2 : 3, then

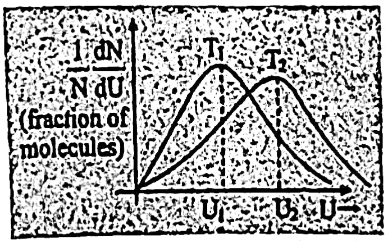
(*a*) The ratio of their molar masses is 16 : 1.

(*b*) The ratio of their molar masses is 1 : 4.

(*c*) The ratio of their moles present inside the container is 1 : 24.

(*d*) The ratio of their moles present inside the container is 8 : 3.

17.



In the above Maxwellian plot at two different temperatures, which of the following statements may be true?

(*a*) Area under the two plots is the same.

(*b*) Fraction of molecules with speed u_1 at T_1 > fraction of molecules having speed u_2 at T_2.

(*c*) $U_2 > U_1$ and $T_2 > T_1$

(*d*) U_{MPS} at $T_1 < U_{MPS}$ at T_2 ; U_{RMS} at $T_1 < U_{RMS}$ at T_2

18. The RMS speeds of the molecules of two gases A and B are in the ratio $\sqrt{3} : 2$ at 27°C for A and 127°C for B. Gases A and B may be respectively:

(*a*) N_2 and CO (*b*) O_2 and N_2H_4

(*c*) N_2O and CO_2 (*d*) SO_2 and SO_3

19. Select correct statements

(*a*) Vapour may be condensed to liquid by the application of pressure.

(*b*) To liquefy a gas one must lower the temperature at or below T_c and apply pressure.

(*c*) At critical conditions there is no distinction between liquid and vapour state.

(*d*) At critical conditions, density of liquid is very high as compared to its gaseous state.

20. Which of the following statement is/are correct?

(*a*) All real gases are less compressible than ideal gas at high pressure.

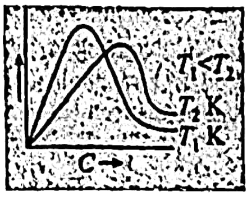
(*b*) Hydrogen and helium are more compressible than ideal gas for all values of pressure.

(*c*) Except H_2 and He, the compressibility factor $Z=\left(\frac{PV}{nRT}\right)<1$ for all gases at low pressure.

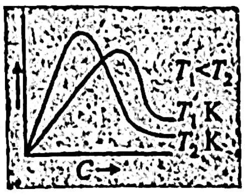
(*d*) The compressibility factor of real gases is independent of temperature.

21. Which of the following graphs are correct for ideal gases?

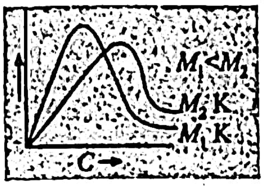
(*a*) $\frac{1}{dC}\left(\frac{dN}{N}\right)$



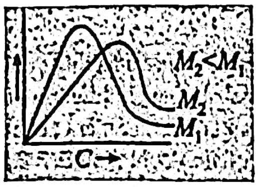
(*b*) $\frac{1}{dC}\left(\frac{dN}{N}\right)$



(*c*) $\frac{1}{dC}\left(\frac{dN}{N}\right)$



(*d*) $\frac{1}{dC}\left(\frac{dN}{N}\right)$



22. Vander Waal's constant 'a' can be expressed as

(*a*) $\frac{9RT_CV_C}{8}$ (*b*) $3P_CV_C^2$

(*c*) $\frac{3}{8}\cdot\frac{P_CV_C}{T_C}$ (*d*) $\frac{27}{64}\cdot\frac{R^2T_C^2}{P_C}$

23. Which of the following statements are correct ?

(*a*) Helium diffuses at a rate 8.65 times as much as CO does.

(*b*) Helium escapes at a rate 2.65 times as fast as CO does.

(*c*) Helium escapes at a rate 4 times as fast as CO_2 does.

(*d*) Helium escapes at a rate 4 times as fast as SO_2 does.

24. Which of the following are correct statements?

(*a*) van der Waals' constant 'a' is a measure of attractive force.

(*b*) van der Waals' constant 'b' is also called co-volume or excluded volume.

(*c*) b is expressed in L mol^{-1}.

(*d*) b is one-third of critical volume.

25. According to the kinetic theory of gases

(*a*) pressure of a gas is due to collisions of molecules with each other.

(*b*) kinetic energy is proportional to square root of the temperature.

(*c*) pressure of a gas is due to collisions of molecules against the sides of the container.

(*d*) there is no force of attraction between gas molecules.

Credit:--- Divansh.....

26. Molecular attraction and size of the molecules in a gas are not negligible at
(*a*) Critical point
(*b*) High pressure
(*c*) High temperature and low pressure
(*d*) low temperature and high pressure

27. Precisely 1 mole of helium and 1 mole of neon are placed in a container. Indicate the correct statements about the system
(*a*) Molecules of the two gases strike the wall of the container with same frequency.
(*b*) Molecules of helium strike the wall more frequently.
(*c*) Molecules of helium has greater average molecular speed.
(*d*) Helium exerts larger pressure.

28. The critical temperature and pressure of a gas are 340 K and 42 atm, respectively. The gas can be liquefied at
(*a*) 340 K and 45 atm (*b*) 340 K and 40 atm
(*c*) 350 K and 100 atm (*d*) 320 K and 42 atm

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 29 to 31): Two containers X & Y are present with container X consisting of some mass of He at some temperature while container Y having double the volume as that of container X & kept at same temperature containing same mass of H_2 gas as the mass of Helium gas. Based on this data & the following conditions, answer the question that follows:

Assume sizes of H_2 molecule & He atom to be same & size of H–atom to be half to that of He–atom & only bimolecular collisions to be occurring.

Condition I: All except one atom of He are stationary in container X & all molecules of H_2 are moving in container Y.

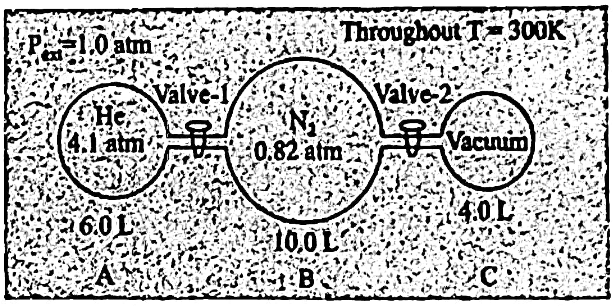
Condition II: Both containers contain all moving molecules.

29. Assuming **condition I** to be applicable & if no. of *total collisions* made by a single molecule in unit time is 'A' in container X, then no. of total collisions made by any one molecule in container Y will be:
(*a*) A (*b*) $\sqrt{3}$A (*c*) $\frac{A}{\sqrt{2}}$ (*d*) A/2

30. Assuming **condition II** to be applicable, the ratio of 'total no. of collisions per unit volume per unit time' in container X & container Y is (container X : container Y)
(*a*) 1 : 1 (*b*) $\sqrt{2}$: 1
(*c*) 1 : $\sqrt{2}$ (*d*) 4 : 1

31. Assuming **condition II** to be applicable, if temperature only of container Y is doubled to that of original (causing dissociation of all H_2 gas into H gaseous atoms) then, if no. of total collisions per unit volume per unit time in container X is A then, no. of 'total collisions made by all molecules per unit volume in container Y would be
(*a*) $2\sqrt{2}$A (*b*) $\sqrt{2}$A
(*c*) $8\sqrt{2}$A (*d*) None of these

Comprehension (Q. 32 to 34): The figure given below shows three glass chambers that are connected by valves of negligible volume. At the outset of an experiment, the valves are closed and the chambers contain the gases as detailed in the diagram. All the chambers are at the temperature of 300K and external pressure of 1.0 atm.

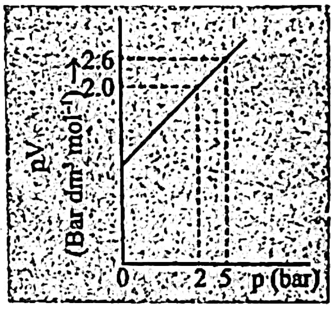


32. Which of the following represents the total kinetic energy of all the gas molecules after both valves are opened?
($R = 0.082$ atm L K^{-1} mol^{-1} = 8.314 L K^{-1} mol^{-1})
(*a*) 2836.2 J (*b*) 3280.0 J
(*c*) 4520.6 (*d*) 4982.4 J

33. Suppose that after both valves are opened, the entire apparatus is cooled to lower the final internal pressure to 1.0 atm. What is the contribution of N_2 gas to this final pressure?
(*a*) 0.40 atm (*b*) 0.35 atm
(*c*) 0.30 atm (*d*) 0.25 atm

34. What is the total pressure in chamber B if only valve–1 is opened?
(*a*) 0.31 atm (*b*) 2.05 atm
(*c*) 2.46 atm (*d*) 3.10 atm

Comprehension (Q. 35 to 36): When intermolecular forces in a real gas are taken zero, variation of pV with pressure p at a given temperature is shown by following isotherm.



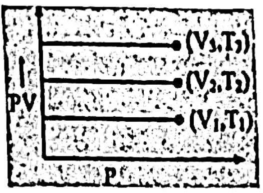
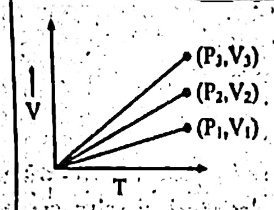
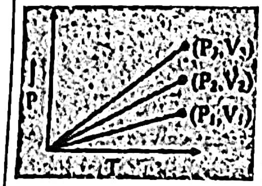
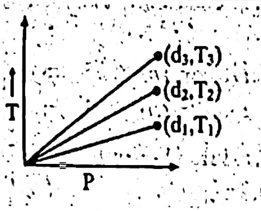
35. Thus, critical volume V_c is
(*a*) 0.2 dm^3 mol^{-1} (*b*) 0.6 dm^3 mol^{-1}
(*c*) 1.8 dm^3 mol^{-1} (*d*) 0.8 dm^3 mol^{-1}

36. If T_c = 100 K for this gas then, p_c is
(*a*) 5.19 bar (*b*) 13.8 bar
(*c*) 41.5 bar (*d*) 55.3 bar

Credit:--- Divansh.....

MATCH THE COLUMN TYPE QUESTIONS

37. For a fixed amount of the gas, match the two columns:

	Column-I		Column-II
A.		p.	$T_3 > T_2 > T_1$
B.		q.	$P_1 > P_2 > P_3$
C.		r.	$V_1 > V_2 > V_3$
D.		s.	$d_1 > d_2 > d_3$

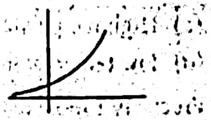
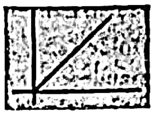
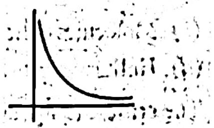
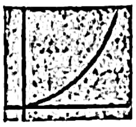
(*a*) A → p, s; B → q, s; C → r; D → p, s
(*b*) A → q, s; B → s; C → r; D → p, r
(*c*) A → s; B → r; C → q, s; D → p, r
(*d*) A → s; B → q, s; C → p, r; D → r

38. Match the column & choose the correct option among the options given.

	Column-I		Column-II
A.	Diffusion of gas	p.	Greater when molecular mass is less
B.	Compressibility of gas (Z) < 1	q.	$V_{real} < V_{ideal}$
C.	V_{rms}	r.	Increases with increase in temperature
D.	Liquefaction of gas	s.	Attractive force dominates

(*a*) A → p, r; B → p, r, s; C → p, r ; D → p, q, s
(*b*) A → p, r; B → q, r, s; C → p, r ; D → q, s
(*c*) A → p, r; B → q, r, s; C → p, q, r; D → p, q, s
(*d*) A → p, r; B → p, q; C → p, q, s; D → p, q, s

39. Match the description in Column-I with graph in Column-II for 'n' moles of an ideal gas at constant temperature & choose the correct option among the options given.

	Column-I		Column-II
A.	P/V vs. P	p.	
B.	P/V vs. V^2	q.	
C.	(V/P) Vs $\frac{1}{P^2}$	r.	
D.	P/V vs. log P	s.	

(*a*) A → r; B → r; C → q; D → p
(*b*) A → s; B → r; C → p; D → q
(*c*) A → s; B → r; C → q; D → p
(*d*) A → r; B → q; C → p; D → s

40. Match the column & choose the correct option among the options given.

	Column-I		Column-II
A.	Critical temperature	p.	Gas can be liquefied.
B.	Boyle's temperature	q.	Deviate from ideal gas equation.
C.	Compressibility factor (Z) < 1	r.	Gas follows the ideal gas equation.
D.	High temperature and low pressure	s.	Assumption of negligible intermolecular force of attraction is valid.

(*a*) A → p, q; B → r, s; C → p, q; D → r, s
(*b*) A → p, r; B → r, s; C → p, r; D → r, s
(*c*) A → r, s; B → p, q; C → r, s; D → p, q
(*d*) A → p, q; B → p, q; C → r, s; D → r, s

41. Match the column & choose the correct option among the options given.

	Column-I		Column-II
A.	Compressibility factor (Z) for ideal gas	p.	$\frac{3}{8}$
B.	Z for real gas at low P	q.	[1 + (Pb/RT)]
C.	Z for real gas at high P	r.	1
D.	Z for critical condition	s.	(1 – a/RTV)

(*a*) A → p; B → s; C → q; D → r
(*b*) A → r; B → q; C → s; D → p
(*c*) A → r; B → s; C → q; D → p
(*d*) A → p; B → q; C → s; D → r

Credit:--- Divansh.....

42. Match the columns & choose the correct option among the options given.

	Column-I		Column-II
A.	H_2 gas at 200 K	p.	Maximum translational K.E. per mol.
B.	CH_4 gas at 400 K	q.	Maximum translational K.E. per gram.
C.	O_2 gas at 900 K	r.	Minimum translational K.E. per mol.
D.	He gas at 600 K	s.	Minimum translational K.E. per gram.

(*a*) A → r; B → p; C → s; D → q

(*b*) A → r; B → q; C → p; D → s

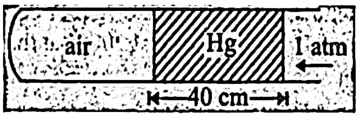
(*c*) A → r; B → p; C → q; D → s

(*d*) A → r; B → s; C → p; D → q

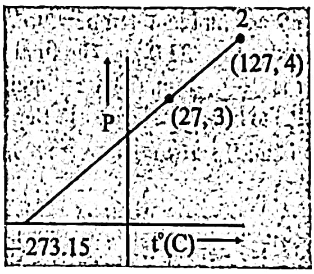
INTEGER TYPE QUESTIONS

43. 500 ml of a vessel contains an ideal gas saturated with water vapours at 3.2 atm and 47°C. Now the entire mass is transferred into vessel of 1800 ml capacity maintained at 87°C. The final pressure **(in atm)** becomes (vapour pressure of water at 47°C and 87°C are 0.2 atm and 0.6 atm, respectively) ________.

44. Air is trapped in a horizontal glass tube of 40 cm mercury column as shown below. If the tube is held vertical keeping the open end up, length of air column shrinks to 19 cm. Length in cm by which the mercury column shifts down is ________.



45. Two moles of an ideal gas undergoes the following process. Given that $\left(\frac{\partial P}{\partial T}\right)_V$ is x × 10^{+y}, then calculate the value of, (x + y)



46. At 1200°C, the following equilibrium is established between chlorine atoms and chlorine molecules: $Cl_2 \rightleftharpoons 2Cl$. The composition of the equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pinhole. It is found that at 1200 °C and 1.8 torr, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the percentage of chlorine molecules dissociated into atoms. [M_{kr} = 83.80 g /mol]

47. An ideal gas, X_n is taken in a container connected to frictionless, massless piston. The pressure of gas is constant (always equal to the atmospheric pressure). The expected graph for the variation of volume of gas with the change in temperature should be like as shown in Fig. I, but the actual graph is like Fig. II. The deviation was attributed to dissociation of gas as $X_n(g) \rightarrow n\,X(g)$. If the yield of this reaction is only 60%, then the value of n is :

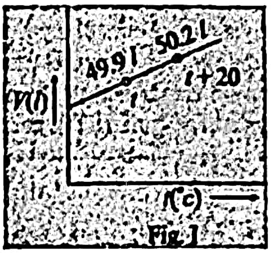


Fig. I

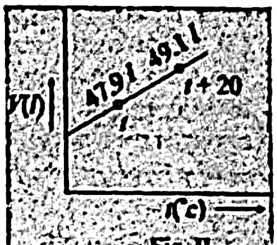


Fig. II

48. A vertical cylinder containing some ideal gas is closed at both ends. A frictionless piston is fitted in the cylinder such that it divides the cylinder into two equal parts at 300K. Moles of gas in lower part is double than that in other part. To what temperature **(in Kelvin)** the cylinder should be heated or cooled such that the volume of upper part becomes three times that of lower part?

49. A gaseous mixture containing equal moles of H_2, O_2 and He is subjected to series of effusion steps. The molar composition (by moles) of effused mixture after 4 effusion steps is x : 1 : y respectively. Then, find the value of $\left(\frac{x}{y}\right)$.

50. Two identical vessels are connected by a tube with a valve letting the gas to pass from one vessel into the other if the pressure difference $\Delta P \geq 2.0$ atm. Initially, there was a vacuum in one vessel while the other contained ideal gas at a temperature 300 K and pressure 4.0 atm. Then both vessels were heated to a temperature 600 K. Up to what value will be the pressure (in atm) in the first vessel (which had a vacuum initially) increase?

51. In a basal metabolism measurement timed at 6.00 min, a patient exhaled 52.5 L of air, measured over water at 20 °C. The barometric pressure was 750 torr. The exhaled air analyzed 16.75 vol% oxygen, and the inhaled air 20.32 vol% oxygen, both on a dry basis. Neglecting any solubility of the gases in water and any difference in the total volumes of inhaled and exhaled air, calculate the rate of oxygen consumption by the patient in mL (STP) per minute.

(The vapor pressure of water at 20°C is 17.5 torr)

52. A container with a volume of 20.0 L holds N_2 (g) and H_2O (l) at 300 K. The pressure is found to be 1.0 atm. The water is then split into di-hydrogen and di-oxygen by electrolysis. After the reaction is complete, the pressure is 1.86 atm. What mass (in g) of water was present initially in the container? The aqueous tension of water at 300 K is 0.04 atm. (R = 0.08 L-atm/K-mol)

Credit:--- Divansh.....

53. Find the number of diffusion steps required to separate the isotopic mixture initially containing some mass of di-hydrogen gas and 1 mole of deuterium (D_2) gas in a 3 litre container maintained at 24.63 atm and 300 K to the final mass ratio of D_2 to H_2 gas equal to 1 : 4.

NUMERICAL TYPE QUESTIONS

54. In order to economize on the oxygen supply in space ships, it has been suggested that the oxygen in exhaled CO_2 be converted to water by a reduction with hydrogen. The CO_2 output per astronaut has been estimated as 1.00 kg per 24 h day. An experimental catalytic converter reduces CO_2 at a rate of 600 mL (STP) per min. What fraction of the time would such a converter have to operate in order to keep up with the CO_2 output of one astronaut? **(Answer upto one decimal place)**

55. For a vander Waal's gas, the volume of gas molecules are negligible. The molar volume of gas is 20 L/mol at 300K. The compressibility factor of the gas is:
[Given: $a = 96\ L^2.atm.mol^{-2}$ and $R = 0.08\ L.atm.mol^{-1}K^{-1}$]
(Answer upto one decimal place)

56. The compressibility factor of 1 mol of Vander waal's gas at 0°C and 100 atm pressure is found to be 1.5. The excluded volume (in L/mol) for the gas will be:
(Answer upto three decimal place)

PYQ's (Past Year Questions)

THE GAS LAWS & IDEAL GAS EQUATION

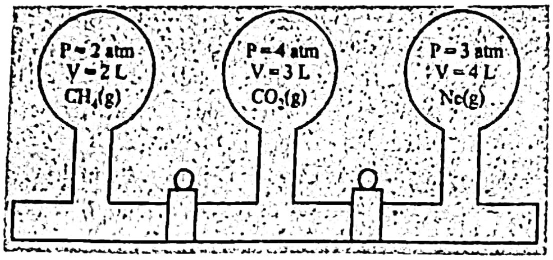
1. A 300mL bottle of soft drink has 0.2 M CO_2 dissolved in it. Assuming CO_2 behaves as an ideal gas, the volume of the dissolved CO_2 at STP is mL. (Nearest integer)
Given: At STP, molar volume of an ideal gas is $22.7\ L\ mol^{-1}$
[30 Jan, 2023 (Shift-I)]

2. At constant temperature, a gas is at a pressure of 940.3 mm Hg. The pressure at which its volume decreases by 40% is _____ mm Hg. (Nearest Integer)
[10 April, 2023 (Shift-I)]

3. The pressure of a moist gas at 27°C is 4 atm. The volume of the container is doubled at the same temperature. The new pressure of the moist gas is __________ $\times 10^{-1}$atm. (Nearest integer) **[25 July, 2022 (Shift-I)]**
(Given: The vapour pressure of water at 27°C is 0.4 atm)

4. An LPG cylinder contains gas at a pressure of 300 kPa at 27°C. The cylinder can withstand the pressure of 1.2×10^6 Pa. The room in which the cylinder is kept catches fire. The minimum temperature at which the bursting of cylinder will take place is __________ °C. (Nearest integer)
[25 July, 2021 (Shift-II)]

5. A spherical balloon of radius 3 cm containing helium gas has a pressure of 48×10^{-3} bar. At the same temperature, the pressure, of a spherical balloon of radius 12 cm containing the same amount of gas will be ____________ $\times 10^{-6}$ bar.
[6 Sept, 2020 (Shift-I)]

6.


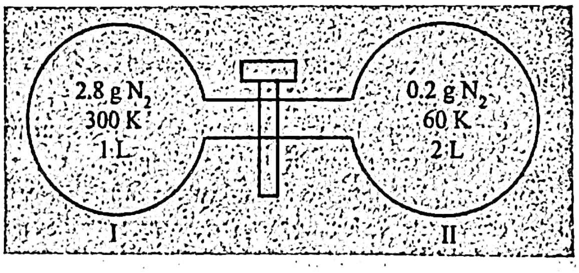
Three bulbs are filled with CH_4, CO_2 and Ne as shown in the picture. The bulbs are connected through pipes of zero volume. When the stopcocks are opened and the temperature is kept constant throughout, the pressure of the system is found to be atm. (Nearest integer) **[8 April, 2023 (Shift-I)]**

7. An evacuated glass vessel weighs 40.0g when empty, 135.0 g when filled with a liquid of density $0.95\ g\ mL^{-1}$ and 40.5 g when filled with an ideal gas at 0.82 atm at 250 K. The molar mass of the gas in $g\ mol^{-1}$ is:
(Given: $R = 0.082\ L\ atm\ K^{-1}\ mol^{-1}$) **[26 June, 2022 (Shift-I)]**
(*a*) 35 (*b*) 50 (*c*) 75 (*d*) 125

8. At 300 K, a sample of 3.0 g of gas A occupies the same volume as 0.2 g of hydrogen at 200 K at the same pressure. The molar mass of gas A is _________ $g\ mol^{-1}$, (nearest integer) Assume that the behaviour of gases as ideal. (Given: The molar mass of hydrogen (H_2) gas is $2.0\ g\ mol^{-1}$.)
[24 June, 2022 (Shift-II)]

9. An empty LPG cylinder weighs 14.8 kg. When full, it weighs 29.0 kg and shows a pressure of 3.47 atm. In the course of use at ambient temperature, the mass of the cylinder is reduced to 23.0 kg. The final pressure inside of the cylinder is ______atm. (Nearest integer)
(Assume LPG to be an ideal gas) **[1 Sept, 2021 (Shift-II)]**

10. Two flasks I and II shown below are connected by a valve of negligible volume.
When the valve is opened, the final pressure of the system in bar is $x \times 10^{-2}$. The value of x is ______. (Integer answer)



Credit:--- Divansh.....

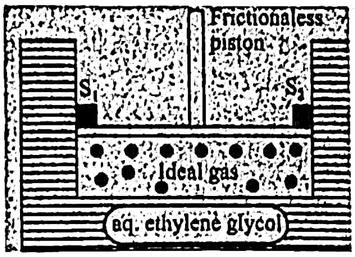
[Assume–Ideal gas; 1 bar = 10^5 Pa; Molar mass of N_2 = 28.0 g mol^{-1} ; R = 8.31 $Jmol^{-1}K^{-1}$]

[27 Aug, 2021 (Shift-II)]

11. A cylinder containing an ideal gas (0.1 mol of 1.0 dm^3) is in thermal equilibrium with a large volume of 0.5 molal aqueous solution of ethylene glycol at its freezing point. If the stoppers S_1 and S_2 (as shown in the figure) are suddenly withdrawn, the volume of the gas in litres after equilibrium is achieved will be _____.

(Given, K_f (water) = 2.0 K kg mol^{-1}, R = 0.08 dm^3 atm K^{-1} mol^{-1})

[9 Jan, 2020 (Shift-II)]



12. 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume 10 m^3 at 1000K. Given: R is the gas constant in JK^{-1} mol^{-1}, x is **[9 Jan, 2019 (Shift-I)]**

(*a*) $\frac{2R}{4+R}$ (*b*) $\frac{2R}{4-R}$ (*c*) $\frac{4+R}{2R}$ (*d*) $\frac{4-R}{2R}$

13. An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is:

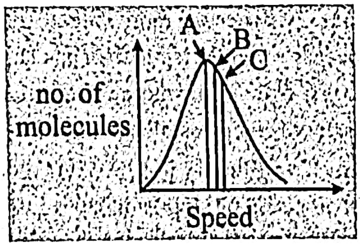
[12 Jan, 2019 (Shift-II)]

(*a*) 500°C (*b*) 500 K (*c*) 750°C (*d*) 750 K

KINETIC MOLECULAR THEORY OF GASES AND MOLECULAR SPEEDS

14. At 600K, the root mean square (rms) speed of gas X (molar mass = 40) is equal to the most probable speed of gas Y at 90K. The molar mass of the gas Y is _______ g mol^{-1}. (Nearest integer) **[12 April, 2023 (Shift-I)]**

15. Identify the correct labels of A, B and C in the following graph from the options given below



Root mean square speed(V_{rms}); most probable speed(V_{mp}); Average speed(V_{av}) **[7 Jan, 2020 (Shift-II)]**

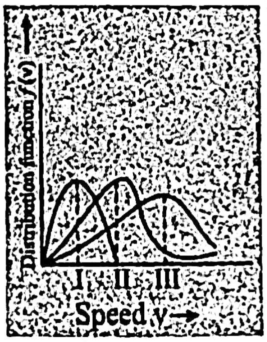
(*a*) A-V_{av}, B-V_{rms}, C-V_{mp} (*b*) A-V_{rms}, B-V_{mp}, C-V_{av}

(*c*) A-V_{mp}, B-V_{rms}, C-V_{av} (*d*) A-V_{mp}, B-V_{av}, C-V_{rms}

16. Points I, II and III in the following plot respectively correspond to

(V_{mp}: most probable velocity)

[10 April, 2019 (Shift-II)]



(*a*) V_{mp} of N_2 (300K); V_{mp} of H_2(300K); V_{mp} of O_2 (400K)

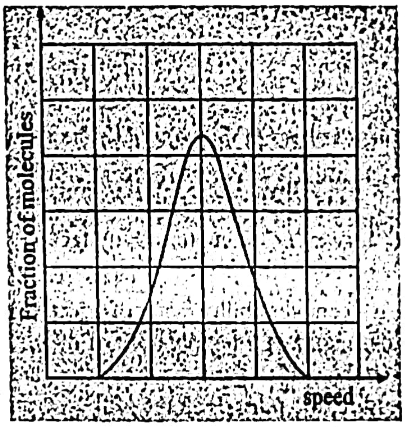
(*b*) V_{mp} of H_2 (300K); V_{mp} of N_2(300K); V_{mp} of O_2(400K)

(*c*) V_{mp} of O_2 (400K); V_{mp} of N_2(300K); V_{mp} of H_2(300K)

(*d*) V_{mp} of N_2 (300K); V_{mp} of O_2(400K); V_{mp} of H_2(300K)

17. If the distribution of molecular speeds of a gas is as per the figure shown below, then the ratio of the most probable, the average and the roots mean square speeds, respectively, is

[JEE Adv 2020]



(*a*) 1 : 1 : 1 (*b*) 1 : 1 : 1.224

(*c*) 1 : 1.128 : 1.224 (*d*) 1 : 1.128 : 1

18. Which of the following statement(s) is (are) correct regarding the root mean square speed (U_{rms}) and average translational kinetic energy (ε_{av}) of a molecule in a gas at equilibrium? **[JEE Adv 2019]**

(*a*) U_{rms} is doubled when its temperature is increased four times.

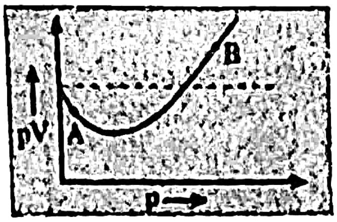
(*b*) ε_{av} at a given temperature does not depend on its molecular mass.

(*c*) U_{rms} is inversely proportional to the square root of its molecular mass.

(*d*) ε_{av} is doubled when its temperature is increased four times.

DEVIATION FROM IDEAL GAS BEHAVIOUR

19. For 1 mol of gas, the plot of pV vs p is shown below. p is the pressure and V is the volume of the gas.



What is the value of compressibility factor at point A?

[29 Jan, 2023 (Shift-I)]

(a) $1-\frac{a}{RTV}$ (b) $1+\frac{b}{V}$

(c) $1-\frac{b}{V}$ (d) $1+\frac{a}{RTV}$

20. A certain quantity of real gas occupies a volume of 0.15 dm^3 at 100 atm and 500 K when its compressibility factor is 1.07. Its volume at 300 atm and 300K (When its compressibility factor is 1.4) is ________ $\times 10^{-4}$ dm^3 (Nearest Integer)

[13 April, 2023 (Shift-I)]

21. For a real gas at 25°C temperature and high pressure (99 bar) the value of compressibility factor is 2, so the value of Vander Waal's constant 'b' should be______ 10^{-2} L mol^{-1}. (Nearest Integer)

(Given R = 0.083 L bar K^{-1} mol^{-1})

[27 July, 2022 (Shift-II)]

22. A certain gas obeys $P(V_m - b) = RT$. The value of $\left(\frac{\partial Z}{\partial P}\right)_T$ is $\frac{xb}{RT}$. The value of x is________.

(Integer answer) (Z : compressibility factor)

[26 Feb, 2021 (Shift-I)]

23. A gas has a compressibility factor of 0.5 and a molar volume of 0.4 dm^3 mol^{-1} at a temperature of 800 K and pressure x atm. If it shows ideal gas behaviour at the same temperature and pressure, the molar volume will be y dm^3 mol^{-1}. The value of x/y is ___.

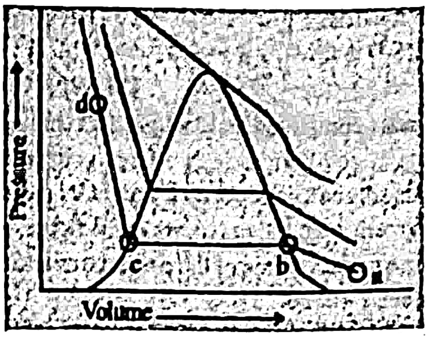
[Use: Gas constant, R = 8×10^{-2} L atm K^{-1} mol^{-1}]

[JEE Adv 2023]

LIQUIFACTION OF GASES AND LIQUID STATE

24. The number of statement's, which are correct with respect to the compression of carbon dioxide from point (a) in the Andrews isotherm from the following is _______.

[24 Jan, 2023 (Shift-II)]



(a) Carbon dioxide remains as a gas upto point (b)

(b) Liquid carbon dioxide appears at point (c)

(c) Liquid and gaseous carbon dioxide coexist between points (b) and (c)

(d) As the volume decreases from (b) to (c), the amount of liquid decreases

25. Consider the van der Waals constants, a and b, for the following gases:

Gas	Ar	Ne	Kr	Xe
a/(atm dm^6 mol^{-2})	1.3	0.2	5.1	4.1
b/(10^{-2} dm^3 mol^{-1})	3.2	1.7	1.0	5.0

Which gas is expected to have the highest critical temperature?

[9 April, 2019 (Shift-I)]

(a) Kr (b) Ne (c) Ar (d) Xe

26. Consider the following table:

Gas	a/(k_{P_a} dm^6 mol^{-1})	b/(dm^3 mol^{-1})
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

a and b are vander waals constant. The correct statement about the gases is:

[10 April, 2019 (Shift-I)]

(a) Gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D.

(b) Gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D.

(c) Gas C will occupy more volume than gas A; gas B will be more compressible than gas D.

(d) Gas C will occupy lesser volume than gas A; gas B will be more compressible than gas D.

PW Challengers

INTEGER TYPE QUESTIONS

1. One mole of a gas changed from its initial state (15L, 2 atm) to final state (4L, 10 atm) reversibly. If this change can be represented by a straight line in P – V curve maximum temperature (approximate), attained by the gas during the process is x × 10^2 K. Then find the value of x.

2. The respiration of the suspension of yeast cells was measured by observing the decrease in pressure of gas above the cell suspension. The apparatus show that the gas was confined to a constant volume, 16.0 ml and the entire pressure change was caused by uptake of oxygen by the cells. The pressure was measured in a manometer, the fluid of which had a density of 1.034 g/cm³. The entire apparatus was immersed in a thermostat at 37°C. In a 30 min observation period the fluid in the open side of the manometer dropped 37 mm. Neglecting the solubility of oxygen in the yeast suspension, if the rate of oxygen consumption by the cells is 10^x mm³ of O_2 (S. T. P) per hour, then find the value of x.

3. A diver at a depth of 10 m exhales some air by which a bubble of air of volume 24.0 ml is formed. The bubble catches an organism which survives on the exhaled air trapped in the bubble. The organism just inhales the air at the rate of 0.05 millimoles/ min and exhales nothing. The atmospheric pressure is 1 atm and the temperature of water is throughout 300 K. The density of water is 1.013 g/ml ($R = 0.08$ L-atm/K-mol, $g = 10\ ms^{-2}$),

   ab = volume (in ml) of bubble when it reaches the surface after 10 minutes,

   cd = average rate (in 10^{-5} mole/min) at which the organism should inhale air so that the volume of bubble remains the same at the depth and at the surface.

   The value of abcd is _________? (10 m $H_2O \cong 1$ atm)

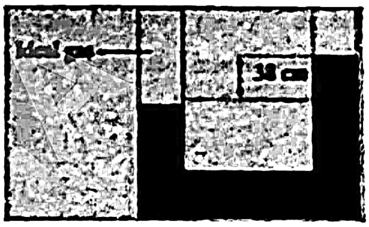
4. A spherical glass bulb of radius 1.0 m contains a concentric rubber balloon that contains some N_2 gas and the remaining space in the flask contains 50 g H_2. In the given conditions, radius of the rubber balloon was found to be 40 cm. Now the seal of glass bulb was opened and 25 g $H_2(g)$ was further added and resealed. Determine radius (in cm) of the rubber balloon in the new conditions. Assume constant temperature throughout.

NUMERICAL TYPE QUESTIONS

5. To maintain the body temperature at 310 K, a Russian Sanyasi breathing his lung capacity once in 5 minutes while meditating in a Himalayan cave where the atmospheric pressure is 70 cm of Hg. After having learnt the art of meditation he goes back home and meditates on the Baltic sea shore where the pressure is 760 torr. Assuming that the atmosphere temperature is 283 K at both the places and that air is composed of 79% N_2 and 21% O_2, calculate his breathing rate (min per breath) required to maintain the body temperature at 310 K at Baltic sea shore. (His O_2 requirement is 3.24 × 10[illegible] molecules per hour). **(Answer upto two decimal place)**

SINGLE CORRECT TYPE QUESTIONS

6. A U-shaped tube partially filled by mercury is taken as shown in the figure. The cross section area of closed arm is A cm² and that of open arm is 2A cm². A pin hole is now made at the top of the closed arm by which leakage of gas starts. The leak rate $\left(\frac{-dP}{dt}\right)$ is directly proportional to the pressure of remaining gas inside the tube over mercury. The proportionality constant is ks^{-1}.



   What will be the increase in level of mercury in the closed arm at any time, t?

   (a) $38(1-e^{-kt})$ cm
   (b) $76(1-e^{-kt})$ cm
   (c) $(1-e^{-kt})$ cm
   (d) $152(1-e^{-kt})$ cm

7. Find the coefficient of thermal expansion, α of an ideal gas in terms of the vander Waal's constants 'a' and 'b'.

   (a) $R\left[PV-\frac{a}{V}+\frac{2ab}{V^2}\right]^{-1}$

   (b) $R\left[PV+\frac{a}{V}+\frac{2ab}{V^2}\right]^{-1}$

   (c) $R\left[PV+\frac{a}{V}-\frac{ab}{V^2}\right]^{-1}$

   (d) $R\left[PV-\frac{a}{V}-\frac{ab}{V^2}\right]^{-1}$

8. Beryllium powder was placed inside a molybdenum vessel with a small effusion hole, 0.318 cm in diameter. At 1537 K, 0.00888 g of Be effused in 15.2 min. Calculate the vapour pressure of Be at 1537 K. Assume the expression $dm = \frac{1}{4}d\bar{c}$ or any equivalent expression, where dm is the mass of the gas effusing, per unit area of cross section; d is the density of the gas and $\bar{c}$ and average speed of the molecules. (Be: Atomic weight = 9.012).

   (a) 3.61×10^{-5} atm
   (b) 2.18×10^{-3} atm
   (c) 4.23×10^{-4} atm
   (d) 5.35×10^{-5} atm

COMPREHENSION BASED QUESTION

The process by which gas passes through a small hole (aperture) into vacuum is called effusion. The rate of change of pressure (p) of a gas at constant temperature and constant external pressure due to effusion of gas from a vessel of constant volume can be related to rate of change of number of molecules by the expression:

$$\frac{dp}{dt} = \frac{kT}{V}\left(\frac{dN}{dt}\right)$$

where rate of change of number of molecules

$$= \frac{dN}{dt} = \frac{-pA_0}{(2\pi mkT)^{1/2}}$$

k (Boltzann constant) = $\frac{R}{N_A}$, R= Ideal gas constant

N_A = Avogadro's number, T = temperature

V = volume of vessel, N = No. of molecules

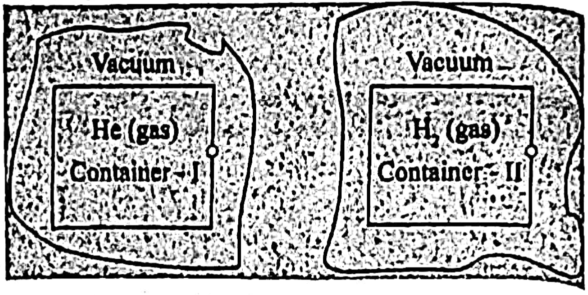
A_0 = area of aperture, m = mass of single molecule

9. Time required for pressure inside vessel to reduce to 1/e of its initial value is (ln e = 1)

(a) $\left(\frac{2\pi m}{kT}\right)^{1/2}\frac{V}{A_0}$ (b) $\left(\frac{kT}{2\pi m}\right)^{1/2}\frac{V}{A_0}$

(c) $\left(\frac{2\pi mkT}{A_0}\right)^{1/2}\frac{V}{A_0}$ (d) $\frac{2\pi m}{kT}\frac{V}{A_0}$

10.



	Container - I	Container-II
Volume of container	1 litre	1 litre
Temperature of container	$\frac{800\pi}{8.314}$(K)	$\frac{1600\pi}{8.314}$(K)
Area of aperture	10^{-7} m²	10^{-6} m²
Time of effusion	1000 sec.	100 sec.
Initial pressure	1 atm	1 atm

The value of $\ln\left(\frac{P_{He}}{P_{H_2}}\right)$ after given time of effusion is

P_{He} = Pressure after 1000 sec. in container - I

P_{H_2} = Pressure after 100 sec. in container - II.

(a) 1 (b) −1

(c) $10\sqrt{10}$ (d) $\frac{1}{10\sqrt{10}}$

> "The best way to capture moments is to pay attention. This is how we cultivate mindfulness."
> – Jon Kabat-Zinn

Credit:--- Divansh.....

ANSWER KEY

CONCEPT APPLICATION

1. (*a*) **2.** (*b*) **3.** (*a*) **4.** (*a*) **5.** (*a*) **6.** (*d*) **7.** (*c*) **8.** (*b*) **9.** (*b*) **10.** (*d*)

11. (*b*) **12.** (*b*) **13.** (*b*) **14.** (*a*) **15.** (*b*) **16.** (*c*) **17.** (*d*) **18.** (*c*) **19.** [12 m] **20.** (*a*)

PRARAMBH (TOPICWISE)

1. (*c*) **2.** (*d*) **3.** (*a*) **4.** (*a*) **5.** (*d*) **6.** (*c*) **7.** (*a*) **8.** (*b*) **9.** (*b*) **10.** (*b*)

11. (*d*) **12.** (*b*) **13.** (*a*) **14.** (*c*) **15.** (*d*) **16.** (*b*) **17.** (*c*) **18.** (*c*) **19.** (*c*) **20.** (*c*)

21. (*c*) **22.** (*c*) **23.** (*a*) **24.** (*a*) **25.** (*d*) **26.** (*b*) **27.** (*b*) **28.** (*d*) **29.** (*a*) **30.** (*a*)

31. (*d*) **32.** (*a*) **33.** (*d*) **34.** (*a*) **35.** (*d*) **36.** (*d*) **37.** (*c*) **38.** (*c*) **39.** (*a*) **40.** (*a*)

41. (*b*) **42.** (*c*) **43.** (*d*) **44.** (*b*) **45.** (*c*) **46.** (*b*) **47.** (*b*) **48.** (*a*) **49.** (*b*) **50.** (*c*)

51. (*c*)

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*b*) **2.** (*a*) **3.** (*b*) **4.** (*c*) **5.** (*d*) **6.** (*a*) **7.** (*c*) **8.** (*d*) **9.** (*d*) **10.** (*b*)

11. (*d*) **12.** (*c*) **13.** (*c*) **14.** (*a,c*) **15.** (*a,d*) **16.** (*b,d*) **17.** (*a,b,c,d*) **18.** (*a,b,c*) **19.** (*a,b,c*) **20.** (*a,c*)

21. (*a,d*) **22.** (*a,b,d*) **23.** (*b,d*) **24.** (*a,b,c,d*) **25.** (*c,d*) **26.** (*a,b,d*) **27.** (*b,c*) **28.** (*a,d*) **29.** (*d*) **30.** (*c*)

31. (*a*) **32.** (*d*) **33.** (*d*) **34.** (*b*) **35.** (*b*) **36.** (*a*) **37.** (*a*) **38.** (*b*) **39.** (*c*) **40.** (*a*)

41. (*c*) **42.** (*d*) **43.** [1] **44.** [10] **45.** [3] **46.** [14] **47.** [6] **48.** [90] **49.** [4] **50.** [3]

51. [280] **52.** [9] **53.** [4] **54.** [58.8] **55.** [0.8] **56.** [0.112]

PYQ's (PAST YEAR QUESTIONS)

1. [1362] **2.** [1567] **3.** [22] **4.** [927] **5.** [750] **6.** [3] **7.** (*d*) **8.** [45] **9.** [2] **10.** [84]

11. [2] **12.** (*d*) **13.** (*b*) **14.** [4] **15.** (*d*) **16.** (*d*) **17.** (*b*) **18.** (*a,b,c*) **19.** (*a*) **20.** [392]

21. [25] **22.** [1] **23.** [100] **24.** [2] **25.** (*a*) **26.** (*c*)

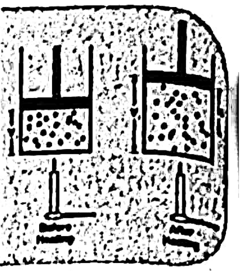
PW CHALLENGERS

1. [7] **2.** [2] **3.** [3610] **4.** [35] **5.** [5.42] **6.** (*b*) **7.** (*a*) **8.** (*a*) **9.** (*a*) **10.** (*c*)

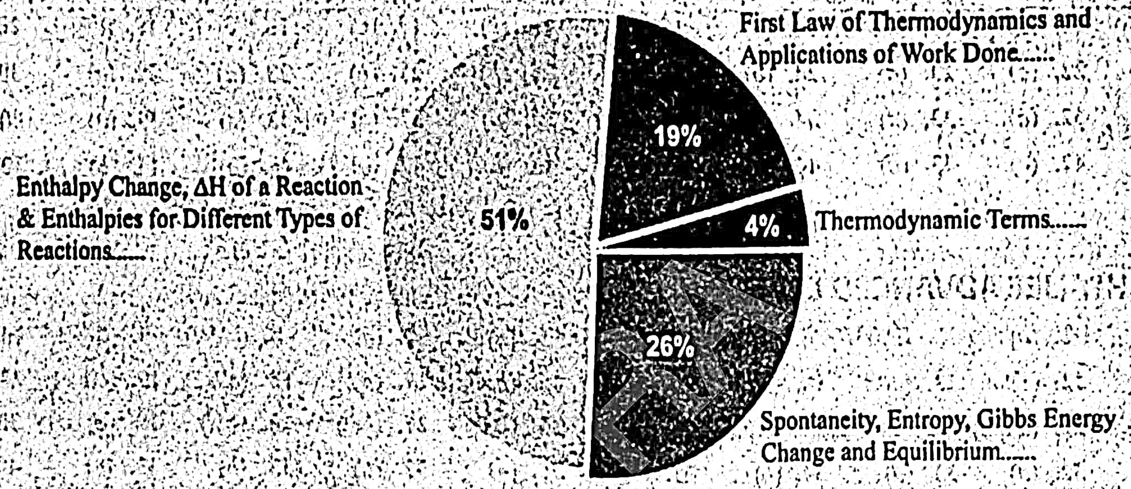
CHAPTER

7

Thermodynamics



Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

INTRODUCTION

Thermodynamics is related with energy and its transformation in various forms in different physical and chemical processes.

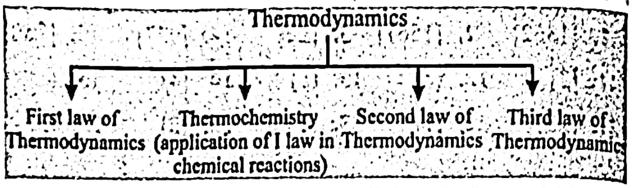
Thermodynamics ≡ Thermo + dynamics

Dynamics ≡ Study of change due to a driving force

Thermo ≡ Thermal which is related to temperature or energy.

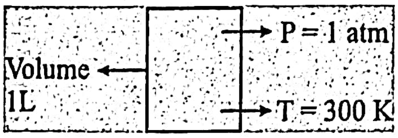
The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

The branch of science which deal with the study of heat energy and its transformation is known as thermodynamics.


Thermodynamics
First law of Thermodynamics
Thermochemistry (application of I law in chemical reactions)
Second law of Thermodynamics
Third law of Thermodynamic

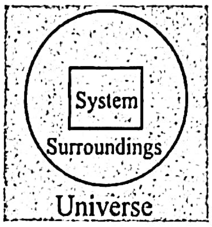
Basic Terms

- **System:** Part of the universe which is under study for energy changes.


P = 1 atm
Volume 1L
T = 300 K

Ex. Air in a room, water in a bottle, any living body.

- **Surrounding:** Rest of the universe.
- **Universe:** Universe = System + Surroundings


System
Surroundings
Universe

Credit:--- Divansh.....

- **Boundary:** Anything which separates system & surroundings is called boundary.
- Boundary can be real or imaginary.
- Boundary can be flexible or rigid

  e.g.: Air in a flexible balloon (flexible boundary)
  Air in a room (fixed boundary).
- Boundary can be adiabatic(non-conducting) or diathermic (conducting).

Classification of System on the Basis of Nature

(*i*) **Homogeneous systems:** A system having uniform nature throughout, (made up of one phase only).

(*ii*) **Heterogeneous system:** A system not uniform throughout, (consists of more than one phase).

Classification of System on the Basis of Boundary

- **Open system:** System which can exchange both energy & matter with the surroundings.

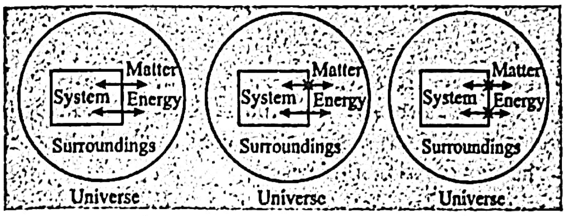
  e.g.: Living systems (any living organism) are open systems, air in an open room.
- **Closed system:** System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.

  e.g.: Any matter in a closed container.
- **Isolated system:** System which cannot exchange both energy as well as matter both with the surroundings.

  e.g.: Water in thermos flask. (Though not a perfectly isolated system but can be taken as isolated system for small interval of time as the energy exchanges are negligible).

Key Note

- Whole of universe is a perfect isolated system.
- An isolated system can be taken as small universe.



Open System Closed System Isolated system

STATE OF A SYSTEM

- It means the condition in which the system is present.
- It can be specified/defined by measuring/specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.

  e.g.: For an ideal gaseous system, state of the system can be defined by specifying volume, temperature and pressure.
- We may have to specify more properties of the system depending on the complexity of the system.

State Function

- Property of a system which is dependent only on the initial & final state of the system i.e., it is a point function.
- It is independent of the path followed to attain a particular state.

Condition for a function to be a state function:

(*i*) If ϕ is state function, $\int_A^B d\phi = \phi_B - \phi_A$

(*ii*) If ϕ is state function, $\oint d\phi = 0$

For any thermodynamic system,

Temperature, Pressure, Volume, Total internal energy (*E* or *U*), Enthalpy(*H*), Gibbs free energy (*G*), Entropy (*S*) are all state functions.

Path Function

- Quantities which are dependent on the path/way, the system has achieved a particular state.

  e.g. Heat, work, Heat capacities (Molar heat capacities, specific heat capacities etc.).
- These quantities are defined when there is a process going on.

TYPES OF PROPERTIES

Extensive Properties

- Functions or properties of the system which are dependent on mass or size of the system are called Extensive Properties.
- Extensive functions are additive in nature e.g. The addition of the volumes of the two parts equals the volume of the whole of the room.

  e.g.: Mass, Total heat capacity, Total internal energy (*E*), Enthalpy(*H*), Gibbs Free Energy(*G*), Entropy(*S*).

Intensive Properties

- Functions or properties which are mass independent or size independent, are called intensive function.
- Intensive properties are not additive in nature.

  eg.: Temperature, pressure, molar heat capacity, specific heat capacity, density, concentration, vapour pressure.

Key Note

How to identify extensive or intensive properties: If a system in a particular state is divided into two equal or unequal parts, the properties which have value equal to the original value of that property for the whole of the system is called an Intensive property. While the properties which have values different from the values for whole of the system are called Extensive Properties.

Train Your Brain

Example 1: Classify the following into open, closed or isolated systems:

(*i*) Animals and plants

(*ii*) A refrigerator or a fridge

(*iii*) A solar cooker

Sol. (*i*) Open system

(*ii*) Closed system

(*iii*) Closed system

Example 2: Which of the following are open, closed or nearly isolated systems?

(*i*) Human beings

(*ii*) The Earth

(*iii*) Can of tomato soup

(*iv*) Ice-cube tray filled with water

(*v*) A satellite in a orbit

(*vi*) Coffee in a thermos flask and

(*vii*) Helium filled balloon.

Sol. Open: Human beings, Earth, Ice cube tray

Close: Can of Tomato soup, A satellite in an orbit, Helium filled balloon.

Isolated: Coffee in thermos flask.

Example 3: Separate out the following into extensive and intensive.

Volume, Temperature, Pressure, Boiling point, Free energy.

Sol. Volume and free energy are extensive, others, are intensive.

Example 4: A thermally isolated gaseous system can exchange energy with the surroundings. What is the mode of transference of energy?

Sol. Work

Concept Application

1. Which amongst the following is an extensive property of the system?

   (*a*) Temperature (*b*) Volume

   (*c*) Viscosity (*d*) Refractive index

2. Which of the following is not a state function of thermodynamic system?

   (*a*) Internal energy(E) (*b*) Free energy(G)

   (*c*) Enthalpy(H) (*d*) Work(W)

3. What is true for a cyclic process [E = internal energy]?

   (*a*) $W = 0$ (*b*) $\Delta E = 0$

   (*c*) $\Delta H = 0$ (*d*) Both (*b*) and (*c*)

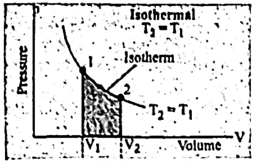
4. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy?

   (*a*) <40kJ (*b*) Zero (*c*) 40kJ (*d*) >40kJ

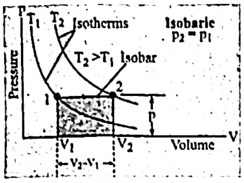
Credit:--- Divansh.....

Types of Processes

(*i*) **Isothermal process:** A process in which temperature of the system remains constant is called isothermal process.

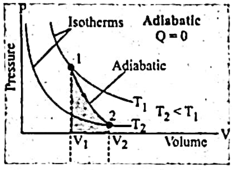


(*ii*) **Isobaric process:** A process in which pressure of the system remains constant is called isobaric process.

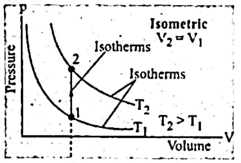


Example: All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

(*iii*) **Adiabatic process:** A process in which no heat exchange takes place is called adiabatic process.



(*iv*) **Isochoric process:** The process for which volume of the system remains constant is called isochoric process i.e., heating of gas in rigid vessel.



(*v*) **Cyclic process:** It is combination of two or more process in which the final state of system, becomes identical to the initial state. The net change in all thermodynamic properties of system must be zero. e.g.,

$\Delta T = \Delta P = \Delta V = \Delta H = \Delta S = \Delta G \ldots\ldots = 0$

However Q_{net} or W_{net} may or may not be zero.

TYPES OF THERMODYNAMIC PROCESSES ON BASIS OF THE WAY THE PROCESSES ARE CARRIED OUT

Reversible Process

- The process that can be reversed by a very small change is known as reversible process.
- Reversible process is carried out in such a manner so that the system is always in thermodynamic equilibrium with the surroundings at every stage of the process.
- Reversible process is carried out such that the difference in driving force and opposing force is infinitesimally small so that process takes place at infinitesimally slow rate.

  $F_{driving} - F_{opposing} = dF$ and $dF \rightarrow 0$
- An ideal reversible process will take infinite time to get completed.
- Strictly speaking there is no ideal reversible process in universe. To get an idea of a reversible process we can consider the following system.

  An ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will be slowing decrease the mass of the sand, lets say, by removing the particles one by one, so the expansion of the gas will take place at infinitesimally small rate and we can always assume the system in thermodynamic equilibrium. So, the expansion will be of reversible type.

Irreversible Process

- The process, which can not be reversed by a small change is known as irreversible process.
- If a process is carried out in such a manner so that the system is in thermodynamic equilibrium
  - (I) Only at initial & final state of the process but not at the intermediate stages.
  - (II) System may be in thermodynamic equilibrium state at some finite number of intermediate stages only. for example - n step irreversible expansion of a gas
- If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate.
- Irreversible processes will get completed in finite time.
- All real process are irreversible.

Work

Thermodynamically, work may be defined as the form of energy which appears only when, there is some change in the boundary of the system. Such work is called mechanical or PV work. Work may also-be non-mechanical like electric work.

Presently, we will discuss only mechanical work.

(*i*) It is not thermodynamic property of system.

(*ii*) Sign convention, work on system = (+)ve.

$$\boxed{W = -\int_{V_1}^{V_2} P_{ext}\,dV}$$

HEAT

Heat is defined as the energy that flows in or out of a system because of a difference in temperature between the system and its surrounding.

According to IUPAC convention:

Heat lost by system is expressed with –ve sign.

Heat given to system is expressed with +ve sign.

- $dq_v = nC_{v,m}dT$
- $dq_p = nC_{p,m}\,dT$
- $C_{p,m} - C_{v,m} = R$ (for ideal gas)

Units of heat & work: Heat and work both are forms of energy. Hence, their SI unit is Joule (J).

$1\ Nm = 1J = 10^7\ erg = 0.239\ cal$
$1\ cal = 4.184\ J = 4.2\ J$
$1\ L\text{-}atm = 101.3\ J = 24.206\ cal = 101.3 \times 10^7\ erg$
$1\ L\text{-}atm > 1\ cal. > 1\ J. > 1\ erg$

INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{Nuclear} + \ldots\ldots\ldots$

U is a state function & is an extensive property.

$\Delta U = U_{final} - U_{initial}$

Characteristics of I.E.

(1) Internal energy of a system is an extensive property.

(2) Internal energy is a state function.

(3) $\Delta U = 0$ (for cyclic process).

- **First law of thermodynamics:** This law was given by Helmholtz and this law can be expressed as follows:
  - (*i*) Energy can neither be created nor be destroyed.
  - (*ii*) The total energy of the universe is always a constant, i.e. the sum of energies of a system and its surrounding is always constant.
  - (*iii*) Whenever a particular form of energy disappears during a process, an equivalent amount of some other form of energy appears.

    $\Delta U = q + w$

HEAT CAPACITY/MOLAR HEAT CAPACITY/ SPECIFIC HEAT CAPACITY

Heat Capacity [C]: The amount of heat required to raise the temperature of a system by 1°C is called heat capacity of system.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temperature}} = \frac{dq}{dT}$$

Units: JK^{-1}, cal K^{-1}, J °C^{-1}, cal °C^{-1}

- Heat capacity is extensive property.

Molar heat capacity: Amount of heat required to raise the temperature of 1 mole substance by 1°C.

Molar heat capacity = heat capacity/mole.

$$\text{Molar heat capacity } (C_m) = \frac{\text{Heat capacity}}{\text{mole of substance}} = \frac{dq}{ndT}$$

$$\Rightarrow \boxed{dq = n.CdT}$$

Units: $Jmol^{-1} K^{-1}$, cal $mol^{-1} K^{-1}$, mol^{-1} °C^{-1}, cal mol^{-1} °C^{-1}

- Molar heat capacity is an intensive property.

Specific heat capacity: Amount of heat required to raise the temperature of 1 gm. of substance by 1°C.

Specific heat capacity = heat capacity/1g of substance.

$$\boxed{c = \frac{C_m}{\text{molecular weight}}} = \frac{dq}{m.dT} \Rightarrow \boxed{dq = m.C.dT}$$

Units: $Jg^{-1} K^{-1}$, cal $g^{-1} K^{-1}$, J g^{-1} °C^{-1}, cal g^{-1} °C^{-1}

- Specific heat capacity is an intensive property.

Key Note

- **Calorie:** Amount of heat required to raise temperature of 1g of water by 1°C (14.5°C to 15.5°C) is called as calorie.
- If heat is supplied at constant pressure, then

$$C_p = \left(\frac{dq}{dT}\right)_p = \frac{dH}{dT} \quad ...(i)$$

- If heat is supplied at constant volume, then

$$C_v = \left(\frac{dq}{dT}\right)_v = \frac{dE}{dT} \quad ...(ii)$$

Key Note

Relation Between C_p and C_v for 1 mole of an ideal gas

$\because$ $H = E + PV$

C_P (always) > C_V

$\therefore$ H = E + nRT (for ideal gas)

$$\left(\frac{dH}{dT}\right) = \left(\frac{dE}{dT}\right) \quad (dH = nC_PdT;\ dU = nC_VdT)$$

$\Rightarrow$ $C_P = C_V + R$

(*i*) $\boxed{C_P - C_V = R}$ Mayer's formula

(*ii*) $\boxed{\frac{C_P}{C_V} = \gamma}$, γ Poisson's ratio

General values of C_v & C_p for an ideal gas can be taken as follows.

Gas	Degree of freedom	$C_{v,m} = \left(\frac{fR}{2}\right)$	$C_{p,m} = \left(\frac{f+2}{2}\right)R$	$\gamma = \left(\frac{f+2}{f}\right)$	Example
Monoatomic	3	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	He; Ne
Diatomic	5	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5}$	N_2;O_2;H_2
Linear polyatomic	5	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5}$	CO_2;HCl
Non Linear polyatomic	6	3R	4R	$\frac{4}{3}$	H_2O; NH_3; CH_4

ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function Enthalpy (H) as.

$H = U + PV$; $\quad \Delta H = \Delta U + \Delta(PV)$

at constant pressure

$\Delta H = \Delta U + P\,\Delta V$

combining with first law.

$\Delta H = q_p$

Hence transfer of heat at constant pressure brings about a change in the enthalpy of the system.

Key Note

If substance is not undergoing chemical reaction or phase change.

$\Delta H = \Delta U + nR\Delta T$ (during heating)

Train Your Brain

Example 5: Calculate the internal energy change in each of the following cases:

(*i*) A system absorbs 5 kJ of heat and does 1 kJ of work.

(*ii*) 5 kJ of work is done on the system and 1 kJ of heat is given out by the system.

Sol. (*i*) Here $q = +5$ kJ and $w = -1$ kJ

$\therefore$ According to first law of thermodynamics, $\Delta E = q + w = 5 + (-1) = 4$ kJ

(*ii*) Here $w = +5$kJ and $q = -1$kJ

$\therefore$ According to first law of thermodynamics $\Delta E = q + w = -1 + (+5) = 4$ kJ

i.e., the internal energy of the system increases by 4 kJ in each case.

Example 6: Represent the following observations in terms of proper IUPAC symbol?

(*a*) Heat absorbed by a system is 20 Joule.

(*b*) Work done by a system is 40 Joule.

(*c*) Work done on a system is 5 Joule.

(*d*) Heat given out by system is 50 Joule.

Sol. It is standard practice to represent both types of heat and work (in/out or on/by) by single symbols q and w

(*a*) $q = +20$ Joule (*b*) $w = -40$ Joule

(*c*) $w = +5$ Joule (*d*) $q = -50$ Joule

Example 7: Predict sign of work done in following reactions at constant pressure.

Initial state		Final state
(i) $H_2O(g)$	→	$H_2O(l)$
(ii) $H_2O(s)$	→	$H_2O(g)$
(iii) $H_2O(l)$	→	$H_2O(s)$
(iv) $CaCO_3(s)$	→	$CaO(s) + CO_2(g)$

Sol. (i) +ve; (ii) –ve; (iii) –ve; (iv) –ve

Concept Application

5. If work done by the system is 300 joule when 100 cal heat is supplied to it. The change in internal energy during the process is

(*a*) –200 Joule (*b*) 400 Joule

(*c*) 720 Joule (*d*) 120 Joule

6. A system has internal energy equal to U_1, 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -

(*a*) $(U_1 + 150\ J)$ (*b*) $(U_1 + 1050\ J)$

(*c*) $(U_1 - 150\ J)$ (*d*) $(U_1 - 1050\ J)$

7. The work done by a system is 8 J when 40 J heat is supplied to it. The change in internal energy of the system during the process is:

(*a*) 32 J (*b*) 40 J

(*c*) 48 J (*d*) –32 J

8. The relation between ΔU and ΔH at constant pressure is

(*a*) $\Delta H = \Delta U - P\Delta V$ (*b*) $\Delta H = \Delta U + P\Delta V$

(*c*) $\Delta U = \Delta V + \Delta H$ (*d*) $\Delta U = \Delta H + \Delta P$

CALCULATION OF Q, W, ΔU & ΔH IN VARIOUS PROCESS

1. Isothermal Expansion or Compression of Ideal Gas

For isothermal process: $\Delta T = 0$, $P_1V_1 = P_2V_2$ = constant (nRT)

$\therefore\ \Delta U = n.C_{v,m}.\Delta T = 0,\ \Delta H = nC_{p,m}\ \Delta T = 0$

and $q = \Delta U - w = -w$

Now, w depends on path (reversible or irreversible).

(*a*) Reversible process

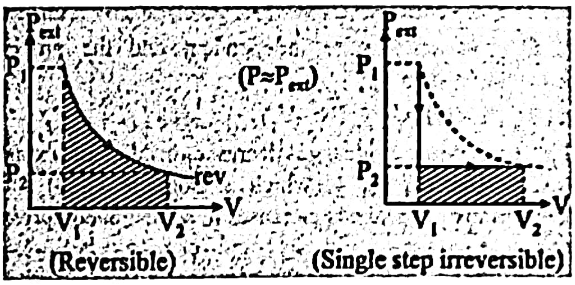
$$w_{rev.} = -\int_{V_1}^{V_2} P_{ext}.dV = -\int_{V_1}^{V_2} \frac{nRT}{V}.dV$$

$$\therefore w_{rev.} = nRT.\ln\frac{V_1}{V_2} = nRT\ \ln\frac{P_2}{P_1}$$

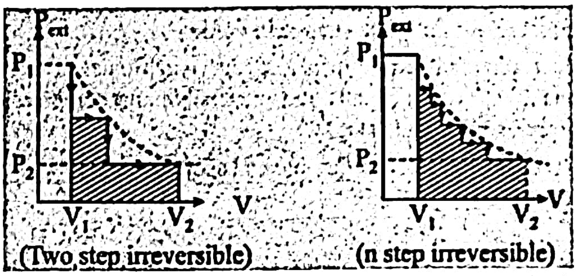
(*b*) Irreversible Process against a Constant External Pressure

$$w_{irr.} = -P_{ext}\int_{V_1}^{V_2} dV = -P_2(V_2 - V_1)$$

❖ **Expansion**



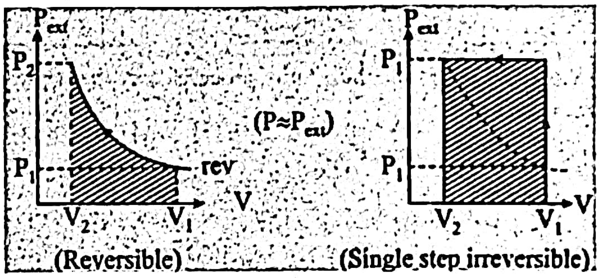
(Reversible) (Single step irreversible)



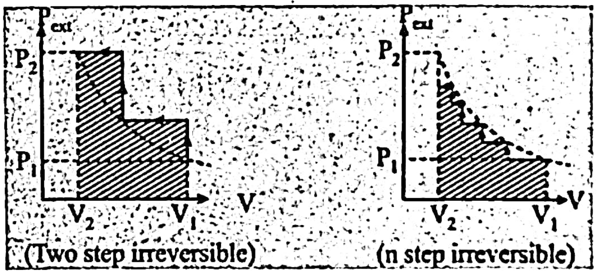
(Two step irreversible) (n step irreversible)

order of value of $(-w_{exp})$: Rev > $\underbrace{\text{n step} > \ldots\ldots > \text{2 step} > \text{single step}}_{\text{irreversible}}$

❖ **Compression**



(Reversible) (Single step irreversible)



(Two step irreversible) (n step irreversible)

Order of value of (w_{comp}) : Rev < $\underbrace{\text{n step} < \ldots\ldots < \text{2 step} < \text{single step}}_{\text{irreversible}}$

2. Free Expansion or Expansion Against Vacuum

$P_{ext} = 0$ but dV = finite, Hence, w = 0

3. Adiabatic Expansion or Compression of Ideal Gas

During adiabatic process, the system acts as isolated or insulated system and hence $q = 0$ in such cases

∴ $\Delta U = w = nC_{v,m}(T_2 - T_1)$

and $\Delta H = nC_{p,m}(T_2 - T_1)$

The change in temperature may be calculated as

$$n\int_{T_1}^{T_2} C_{v,m}\,dT = -\int_{V_1}^{V_2} P_{ext}\,dV$$

(a) If $C_{v,m}$ is temperature independent and the process is reversible, then

$T.V^{\gamma-1}$ = constant

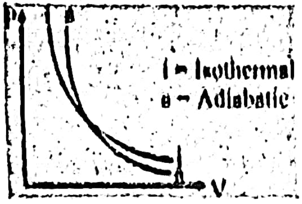
or, $P.V^{\gamma}$ = constant

or, $T^{\gamma}P^{1-\gamma}$ = constant

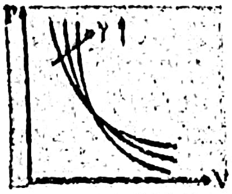
(b) If $C_{v,m}$ is temperature independent and the process is irreversible, then

$n.C_{v,m}(T_2 - T_1) = -P_{ext}(V_2 - V_1)$

- The temperature of ideal gas decreases in adiabatic expansion (except free expansion, which is isothermal too) and the temperature of ideal gas increases in adiabatic compression.
- The final temperature of gas is always higher in irreversible process (expansion or compression) relative to reversible process, for the same change in volume.
- Just like isothermal process, the magnitude of work is maximum when expansion is reversible and compression is irreversible (single step).
- Work in reversible isothermal and adiabatic processes may be compared graphically.



- Work in reversible adiabatic process may be compared graphically.



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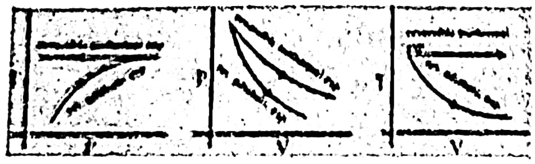


Comparison of reversible adiabatic expansion and reversible isothermal expansion on TP, PV and TV diagram.

- During reversible adiabatic process:

Work of expansion in adiabatic reversible process

$W = -\int_{V_1}^{V_2} PdV$

For adiabatic process $PV^{\gamma} = P_1V_1^{\gamma} = P_2V_2^{\gamma}$ = constant (K)

or $P = \frac{K}{V^{\gamma}}$

$$\therefore W = -\int_{V_1}^{V_2}\frac{K.dV}{V^{\gamma}} = -K\int_{V_1}^{V_2}\frac{dV}{V^{\gamma}} = \frac{-1}{1-\gamma}\left(KV_2^{1-\gamma} - KV_1^{1-\gamma}\right)$$

But $P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$

$$\therefore W = \frac{-1}{1-\gamma}\left(P_2V_2^{\gamma}.V_2^{1-\gamma} - P_1V_1^{\gamma}.V_1^{1-\gamma}\right)$$

$$= \frac{-1}{1-\gamma}(P_2V_2 - P_1V_1) = \frac{-1}{1-\gamma}(nRT_2 - nRT_1)$$

or $\boxed{W = \frac{-nR(T_2 - T_1)}{1-\gamma}}$ here $\gamma = \frac{C_P}{C_V}$

C_P and C_V are molar heat capacities at constant pressure and volume respectively.

from Mayer's relation $C_P - C_V = R$

∵ $\frac{C_P}{C_V} = \gamma$ ∴ $C_P = C_V \times \gamma$

∴ $C_V \times \gamma - C_V = R$ or $C_V(\gamma - 1) = R$

or $-C_V(1-\gamma) = R$ or $C_V = -\frac{R}{1-\gamma}$

so $\boxed{W = nC_V(T_2 - T_1)}$

4. Isobaric Process for an Ideal Gas

$\Delta P = 0 \Rightarrow \frac{V}{T}$ = constt.

$w = -P.(V_2 - V_1) = -nR.\Delta T$

Let the energy given to system is q and work done by the system is W, then Internal energy $\Delta U = q_p - w$

Here, q_p = energy given to system at constant pressure

So $q_p = \Delta U + W$ ...(1)

$q_p = (U_2 - U_1) + P(V_2 - V_1)$

$q_p = (U_2 + PV_2) - (U_1 + PV_1)$

$q_p = H_2 - H_1$ {∵ $H = U + PV$ = enthalpy}

$q_p = \Delta H = n.C_{p,m}.\Delta T$

∴ $\Delta U = n.C_{v,m}.\Delta T$

5. Isochoric Process for an Ideal Gas

$\Delta U = 0 \Rightarrow \frac{P}{T}$ = constt.

$w = 0$

$q = \Delta U = n.C_{v,m}.\Delta T$

∴ $\Delta U = n.C_{v,m}.\Delta T$

Thus during isochoric process, heat supplied to the system is equal to change in internal energy.

6. Polytropic Process for an Ideal Gas

$\Delta U = n.C_{v,m}.\Delta T$

∴ $\Delta H = n.C_{p,m}.\Delta T$

$P.V^{x}$ = constant

or, $T.V^{x-1}$ = constant

where x = polytropic index

$$w_{poly} = \frac{P_2V_2 - P_1V_1}{1-x} = \frac{nR(T_2 - T_1)}{1-x} \qquad (x \neq 1)$$

$$= -nRT \ln \frac{V_2}{V_1} \qquad (x = 1)$$

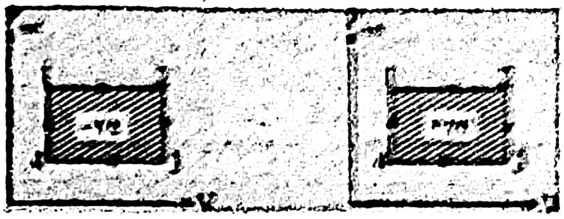
and $q = nC_n\Delta T$

The molar heat capacity, $C_n = C_{v,m} + \frac{R}{1-x}$

7. Cyclic Process

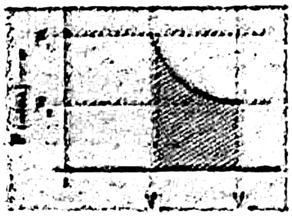
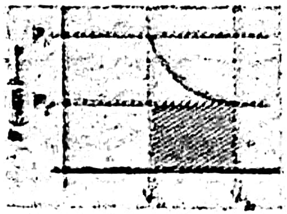
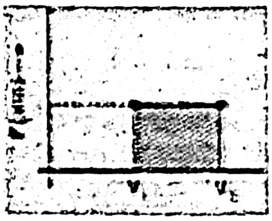
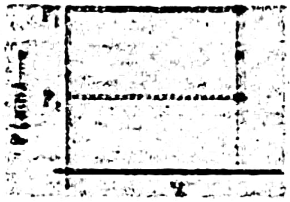
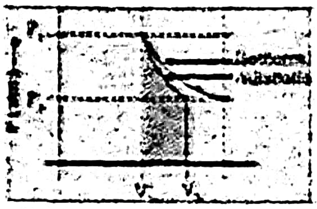
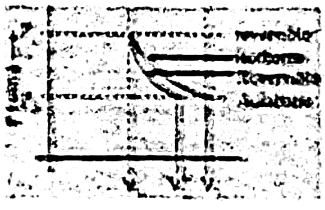
$\Delta U = 0$, so $q = -w$

i.e., work done by the system is equal to heat absorbed by the system.

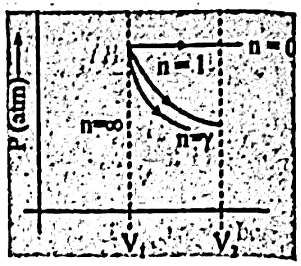
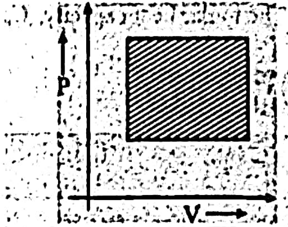


Sign of net work done in cyclic process

SUMMARY

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln\left(\frac{V_2}{V_1}\right)$ $q = nRT \ln\left(\frac{P_1}{P_2}\right)$	0	0	
Irreversible isothermal	$w = -P_{ext}(V_2-V_1)$ $= -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$	$q = P_{ext}(V_2-V_1)$	0	0	
Isobaric process	$w = -P_{ext}(V_2-V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_{p,m}\Delta T$	$\Delta U = nC_{V,m}\Delta T$	$\Delta H = nC_{p,m}\Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_{V,m}\Delta T$	$\Delta U = nC_{V,m}\Delta T$	$\Delta H = nC_{p,m}\Delta T$	
Reversible adiabatic process	$w = nC_{V,m}(T_2-T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $PV^{\gamma} = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma} = \text{constant}$	$\Delta U = nC_{V,m}\Delta T$	$\Delta H = nC_{p,m}\Delta T$	
Irreversible adiabatic process	$w = nC_{V,m}(T_2-T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $nC_{V,m}(T_2-T_1)$ $= P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$	$\Delta U = nC_{V,m}\Delta T$	$\Delta H = nC_{p,m}\Delta T$	

Credit:--- Divansh.....

Polytropic	$w = \frac{P_2V_2 - P_1V_1}{n-1}$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$q = n\,C_V dT$ $C = C_V + \frac{R}{1-n}$	$\Delta U = nC_{V,m}\Delta T$	$\Delta H = nC_{P,m}\Delta T$	
Cyclic Process	Area enclosed in PV-diagram (For clockwise –ive, For anticlockwise +ive)	$q = -w$	0	0	

Train Your Brain

Example 8: 500 joule of heat was supplied to a system at constant volume. It resulted in the increase of temperature of the system from 20°C to 25°C. What is the change in internal energy of the system?

Sol. $\Delta E = 500$ J at constant vol. $(\Delta E = q_v)$

Example 9: Two moles of an ideal gas ($\gamma = 1.2$) is heated from 27°C to 47°C at constant volume. Calculate q, ΔU, w and ΔH.

Sol. $w = 0$

$$q = \Delta U = n.C_{v,m}\Delta T = 2\times\frac{R}{1.2-1}\times 20 = 200R$$

$$\Delta H = \gamma.\Delta U = 240R$$

Example 10: Two moles of an ideal gas undergoes isothermal expansion from 4L to 20L at 27°C. Calculate q, w, ΔU and ΔH, if the process is performed.

(*i*) Reversibly

(*ii*) Irreversibly, against a constant external pressure of 1 atm.

(*iii*) As free expansion

Sol. For isothermal process, $\Delta T = 0$.

Hence,

$\Delta U = n.C_{v,m}.\ \Delta T = 0$

$\Delta H = n.C_{p,m}.\ \Delta T = 0$

(*i*) $w = -nRT.\ln\frac{V_2}{V_1} = -2\times 8.314\times 300\times\ln\frac{20}{4} = -8030.31J$

and $q = -w = 8030.31$ J

(*ii*) $w = -P_{ext}(V_2 - V_1) = -1$ atm (20L–4L) = –16L-atm

$= -16\times 101.3$ J $= -1620.8$ J

$q = -w = 1620.8J$

(*iii*) $w = 0$ and $q = 0$

Example 11: Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm, against a constant external pressure of 1 atm. If the initial temperature of gas is 27°C, calculate the final temperature. Also calculate q, ΔU, w and ΔH.

Sol. $q = 0$

$\Delta U = w,$

or, $n.C_{v,m.}(T_2 - T_1) = -P_{ext}.(V_2 - V_1)$

or, $n.\frac{3}{2}R(T_2 - T_1) = -P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$

or, $\frac{3}{2}(T_2 - 300) = -\left(T_2 - 300\times\frac{1}{12}\right) \Rightarrow T_2 = 190K$

or, $\Delta U = w = 5\times\frac{3}{2}R\times(190-300) = -6859.05J$

and $\Delta H = \gamma.\Delta U = -11431.75J$

Example 12: A gas occupies 2 litre at S.T.P. It is provided 300 joule heat so that its volume becomes 2.5 litre at 1 atm. Calculate change in its internal energy.

Sol. Given $V_1 = 2$ litre, $V_2 = 2.5$ litre,

$q = +300J,\ P_{external} = 1$ atm.

$\therefore\ \Delta E = q + W$

$W = -P_{external}\,\Delta V = -P_{external}(V_2 - V_1)$

$= -1$ atm × (2.5–2) litre = –0.5 litre atm.

$W = -0.5\times 101.3\ J = -50.65J$

$\therefore\quad \Delta E = q + W = 300 + (-50.65) = 249.35$ J

Example 13: Two litre of N_2 at 0°C and 5 atm are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming the gas to be ideal calculate work of expansion?

Sol. Given $P_1 = 5$ atm, $V_1 = 2$ litre, $P_2 = 1$ atm, $V_2 = ?$

We know that - if T is constant then $P_1V_1 = P_2V_2$

$\Rightarrow V_2 = \frac{P_1V_1}{P_2} = \frac{5\times 2}{1} = 10$ litre

$W = -P_{ext}\,\Delta V = -1(V_2 - V_1) = -1(10-2) = -8$ litre atm $= -8\times 101.3 = -810.4$ joule

Concept Application

9. Which of the following statement is false?
   (*a*) Work is a state function.
   (*b*) Temperature is a state function.
   (*c*) Change of state is completely defined when initial and final states are specified.
   (*d*) Heat & work appears at the boundary of the system and surrounding.

10. One mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95K) to (4.0 atm, 5.0 L 245 K) with a change in internal energy (ΔU) = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm.
    (*a*) 40.0
    (*b*) 42.3
    (*c*) 44.0
    (*d*) Not defined, because pressure is not constant.

11. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in KJ) for the process is:
    (*a*) 11.4 kJ (*b*) −11.4 kJ
    (*c*) 0 kJ (*d*) 4.8 kJ

12. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temperature.
    ($R = 0.0821$ litre, alm K^{-1} mol^{-1})
    (*a*) T (*b*) $\dfrac{T}{(2)^{\frac{5}{3}-1}}$
    (*c*) $T-\dfrac{2}{3\times0.0821}$ (*d*) $T+\dfrac{2}{3\times0.0821}$

13. Two moles of an ideal gas expand spontaneously into vacuum. The work done is:
    (*a*) Zero (*b*) 2 J (*c*) 4 J (*d*) 8 J

THERMOCHEMISTRY

Physicochemical changes are classified as endothermic, accompanied by absorption of heat and exothermic, accompanied by the evolution of heat.

For exothermic reactions ($q < 0$)

At constant pressure, $\Delta H = (H_P - H_R) = -ve$ $(\because H_P < H_R)$

At constant volume, $\Delta E = (E_P - E_R) = -ve$ $(\because E_P < E_R)$

For endothermic reaction, ($q > 0$)

At constant pressure, $\Delta H = (H_P - H_R) = +ve$ $(\because H_P > H_R)$

At constant volume, $\Delta E = (E_P - E_R) = +ve$ $(\because E_P > E_R)$

Like any other transfer of heat, the heat change of a chemical reaction depends upon the conditions during the process by which it is carried out.

Key Note

I: $\Delta U = q_V$

This condition is excellently approximated when the reaction is carried out in a bomb calorimeter, where the volume remains constant.

II: During the course of an experiment under ordinary bench-top conditions, the pressure is kept constant. Many calorimeters operate at constant atmospheric pressure. Then, we have

$\Delta H = q_P$

The heat of reaction measured at constant pressure is exactly equal to the change in enthalpy of the reaction system.

Constant pressure processes are much common in chemistry. Therefore, usually when ever we speak of heat of reaction, it implies enthalpy change at constant pressure.

It is often necessary to use data obtained with bomb calorimeter which give ΔE in order to calculate ΔH.

We know that, $\Delta H = \Delta U + \Delta(PV)$

- If all the reactants and products are liquids or solids, the PV values change only slightly so $dU = dH$.
- For reactions in which gases are involved, the values of $\Delta(PV)$ depends on the change in the number of moles of gas as a result of reaction.

$\therefore \Delta(PV) = \Delta n_g(RT)$

$\therefore \Delta H = \Delta U + \Delta n_g RT$

Enthalpy of a Substance

- Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value. Only the change in enthalpy can be calculated when substance is taken from one state to other.
- The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol H_m(substance): For example molar enthalpy of water vapours at 398 K and 1 atm pressure may be represented as H_m (H_2O, g, 398 K, 1 atm). In very simple words, enthalpy can be considered as heat content (amount) of substance, and during reaction this heat is being released or absorbed.
- Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance.

Standard State of any Substance Means

- For a **GAS**, standard state means ideal gas at 1 bar partial pressure at any give temperature.
- For a **LIQUID** – pure liquid at 1 bar pressure at any given temperature.
- For a **PURE CRYSTALLINE SOLID** – pure crystalline solid at 1 bar pressure and at any given temperature
- For any **SUBSTANCE** or **ION IN SOLUTION** – the species should be in unit molality, at one bar pressure and at any given temperature.

Credit:--- Divansh.....

ENTHALPY OF REACTION

It is defined as the amount of heat evolved or absorbed when the reacting species, as represented by a balanced chemical equation have completely reacted.

Enthalpy or heat of reaction is given by:

$$\Delta H_{reaction} = \Sigma(\Delta H_f)_{product} - \Sigma(\Delta H_f)_{reactant}$$

FACTORS AFFECTING HEAT OF REACTION

(*i*) **Physical state of Reactants and Products:** Physical state always affects the heat of reaction as heat energy is involved in changing the physical state of a substance. For example,

$H_2(g) + ½\,O_2(g) \longrightarrow H_2O(g);\ \Delta H = -57.8$ kcal/mol

$H_2(g) + ½\,O_2(g) \longrightarrow H_2O(l);\ \Delta H = -68.32$ kcal/mol

Difference in the value of ΔH is observed because heat is evolved when steam condenses.

Allotropic forms of The Elements: The value of ΔH also depends on the allotropic form used in the reaction. For example,

$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -94.3$ kcal/mol

$C(\text{amorphous}) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -97.6$ kcal/mol

The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is called heat of transition.

$C(\text{diamond}) \longrightarrow C(\text{amorphous});\ \Delta H = 3.3$ kcal/mol

(*ii*) **Enthalpies of Solution:** Enthalpies of solution differ depending on whether the substances react together in dry state or in solution. For example,

$H_2S(g) + I_2(g) \longrightarrow 2HI(\text{solution}) + S(s)\ \Delta H = -17.2$ kcal/mol

$H_2S(g) + I_2(\text{solution}) \longrightarrow 2HI\ (\text{solution}) + S(s)$

$\Delta H = -21.93$ kcal/mol

(*iii*) **Temperature:** Enthalpy change of reaction also depends on temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature.

Key Note

- Relation between ΔH or ΔE and temperature are given by **Kirchoff's equation.**

$$(\Delta H_2 - \Delta H_1) = \Delta C_P\,(T_2 - T_1)$$

$$(\Delta E_2 - \Delta E_1) = \Delta C_V\,(T_2 - T_1)$$

$$\boxed{\frac{\Delta H_{T_2} - \Delta H_{T_1}}{(T_2 - T_1)} = \Delta C_P}$$

This equation is used to find heat change of reaction at a temperature when it is known at another temperature.

Similarly, $\boxed{\dfrac{\Delta E_{T_2} - \Delta E_{T_1}}{(T_2 - T_1)} = \Delta C_V}$

LAWS OF THERMO CHEMISTRY

(*a*) **Lavosier and Laplace's law:** Enthalpy of decomposition of a compound is numerically equal to the formation of that compound and only sign changes.

(*b*) **Hess's Law:** The total amount of heat evolved or absorbed in a chemical reaction is the same whether the reaction is carried out in one or several steps (by one or more methods).

It also does not depend upon the manner in which the chemical reaction is carried out.

Ex. Single step reaction $A \rightarrow B;\ \Delta H$

Multi step reaction to produce B from A is given

$$A \xrightarrow{\Delta H_1} C \xrightarrow{\Delta H_2} D \xrightarrow{\Delta H_3} E \xrightarrow{\Delta H_4} B$$

According to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

ENTHALPY OF FORMATION

The amount of heat evolved or absorbed when one mole of a substance is formed from its constituent elements in their most stable state is called heat of formation.

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g);\ \ \Delta H = -44$ kcal/mol

Thus, enthalpy of formation of HCl is –22 kcal/mol

The formation reaction of a compound has only one mole of the compound and nothing else on the product side. Only elements in their stable states of aggregation appear on the reactant side.

$$H^\circ_T = H^\circ_{298} + \int_{298}^{T} C^\circ_P\,dT$$

This expression holds good for both elements as well as compounds. For elements, the first term on the right hand side is zero.

Enthalpy of Reaction from Enthalpies of Formation: The enthalpy of reaction can be calculated by.

$$\Delta H_r^\circ = \Sigma\,\nu_B\,\Delta H^\circ_{f,(\text{products})} - \Sigma\,\nu_B\,\Delta H^\circ_{f,(\text{reactants})}$$

where ν_B denotes corresponding stoichiometric coefficient

Enthalpy of Formation of Elements

- "By convention, the standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value." The specified temperature is usually taken as 25°C.

A few examples are $\Delta H_f^\circ\,(O_2, g) = 0$

ΔH_f° (C, graphite) = 0

ΔH_f° (Br_2, liquid) = 0

ΔH_f° (S, rhombic) = 0 $\qquad \Delta H_f^\circ$ (S, monoclinic) ≠ 0

ΔH_f° (P, white) = 0 $\qquad \Delta H_f^\circ$ (P, black) ≠ 0

- "The standard enthalpy of formation of a compound is the change in the standard Enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation."

Train Your Brain

Example 14: For the reaction : $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$

if $\Delta U^\circ = -1373$ kJ mol^{-1} at 298 K. Calculate ΔH°

Sol. –1368 kJ mol^{-1}

$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$

$$\Delta H^\circ = -1373 + \frac{2\times 8.314\times 298}{1000}$$

$$\Delta H^\circ = -1368 \text{ kJ mol}^{-1}$$

Example 15: Classify the following processes as exothermic or endothermic:

(*a*) Burning of a match stick

(*b*) Melting of ice

(*c*) Molten metal solidifies

(*d*) Reaction between Na and H_2O

(*e*) Rubbing alcohol evaporates.

Sol. Exothermic *a*, *c*, *d*; Endothermic : *b*, *e*

Example 16: Calculate heat change of the following reaction at constant pressure,

$F_2O(g) + H_2O(g) \rightarrow O_2\,(g) + 2HF(g)$

The heats of formation of F_2O (g), mol $H_2O(g)$ and HF (g) are 5.5 kcal/mol, –57kcal/mol and –64 kcal/mol respectively.

Sol. Given that

$$\Delta H_{reaction} = \Sigma(\Delta H_f)_{product} - \Sigma(\Delta H_f)_{reactant}$$

$$\Sigma H_{reaction} = [\Delta H_f(O_2) + 2\Delta H_f(HF)] - [\Delta H_f(F_2O) + \Delta H_f(H_2O)]$$

$$= [0 + (-64)\times 2] - [-5.5 - 57]$$

$$= -65.5 \text{ Kcal/mol}$$

Concept Application

14. A mixture of 2 mole of CO and 1 mole of O_2, in a closed vessel is ignited to convert the CO to CO_2. If ΔH is the enthalpy change and ΔU is the change in internal energy then:

(*a*) ΔH > ΔU $\qquad$ (*b*) ΔH = ΔU

(*c*) ΔH < ΔU $\qquad$ (*d*) None of these

15. Consider the following changes:

(I) $\frac{1}{2}H_2(g) + aq. \longrightarrow H^+(aq.)$

(II) $2O(g) \longrightarrow O_2(g)$

(III) $NH_4^+(g) + Cl^-(g) \longrightarrow NH_4Cl(s)$

(IV) $P_4(\text{black}) + 5O_2(g) \longrightarrow P_4O_{10}(s)$

Which of the above does not represent $\Delta H^\circ_{\text{formation}}$ of the product?

(*a*) II, III $\qquad$ (*b*) I, IV

(*c*) I, II, III $\qquad$ (*d*) II, III, IV

ENTHALPY OF COMBUSTION

- It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.

  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)\ \Delta H^\circ = -890\ kJ\ mol^{-1}$

Key Note

- **Calorific value:** The amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised is called calorific value of food for fuel.

  When one mole of methane burns, 890.3 kJ of energy is released.

  So, the calorific value of methane $= -\frac{890.3}{16} = -55.6 kJ/g$

Train Your Brain

Example 17: The standard heats of formation of $CH_4(g)$ $CO_2(g)$ and $H_2O(g)$ are –76.2, –398.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal conditions.

Sol. The required equation for the combustion of methane is:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O;\ \Delta H = ?$$

$$\Delta H = \Delta H_{f(products)} - \Delta H_{f(reactants)}$$

$$= \Delta H_{f(CO_2)} + 2 \times \Delta H_{f(H_2O)} - \Delta H_{f(CH_4)} - 2\Delta H_{f(O_2)}$$

$$= -398.8 - 2 \times 241.6 - (-76.2) - 2 \times 0$$

$$= -805.8\ kJ\ mol^{-1}$$

Heat evolved by burning 22.4 litre (1 mole) methane = 805.8 kJ. So, heat evolved by burning 1000 litre ($1 m^3$) methane.

$$= \frac{805.8}{22.4} \times 1000 = 35973.2 kJ$$

Concept Application

16. The heat of combustion of ethyl alcohol is –300 kcal/mol. If the heats of formation of CO_2 (g) and $H_2O(\ell)$ are –94.3 and –68.5 kcal/mol respectively, calculate the heat of formation of ethyl alcohol.

(*a*) – 94.1 kcal/mol (*b*) – 64.1 kcal/mol

(*c*) – 96.1 kcal/mol (*d*) – 59.1 kcal/mol

17. The standard heat of combustion of solid boron is equal to:

(*a*) $\Delta H_f^\circ (B_2O_3)$ (*b*) $(1/2)\, \Delta H_f^\circ (B_2O_3)$

(*c*) $2\Delta H_f^\circ (B_2O_3)$ (*d*) $(3)\, \Delta H_f^\circ (B_2O_3)$

18. Which one of the following expresses Q as the heat of combustion?

(*a*) $2H_2 + O_2 \longrightarrow 2H_2O + Q$

(*b*) $C + \frac{1}{2}O_2 \longrightarrow CO + Q$

(*c*) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + Q$

(*d*) $2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O + Q$

ENTHALPY OF SOLUTION

The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration.

While recording integral enthalpies of solution it is a general ctice to state the amount of the solvent in which 1 mole of ute is dissolved; Thus

$HCl(g) + 10H_2O(\ell) \rightarrow HCl{\cdot}10H_2O$

$\Delta H = -69.5\ kJ\ mol^{-1}$

indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are:

(*i*) $HCl(g) + 25\ H_2O(\ell) \rightarrow HCl.25H_2O$ $\quad \Delta H_2 = -72.3\ kJ\ mol^{-1}$

(*ii*) $HCl(g) + 40\ H_2O(\ell) \rightarrow HCl.40H_2O$ $\quad \Delta H_3 = -73.0\ kJ\ mol^{-1}$

(*iii*) $HCl(g) + 200\ H_2O(\ell) \rightarrow HCl.200H_2O$ $\quad \Delta H_4 = -74.2\ kJ\ mol^{-1}$

(*iv*) $HCl(g) + aq \rightarrow HCl\ (aq)$ $\quad \Delta H_5 = -75.0\ kJ\ mol^{-1}$

Key Note

- Whenever amount of solvent is not specified then take its amount to be very large just like in equation no. (*iv*).

ENTHALPY OF HYDRATION

Enthalpy of hydration is used in following two ways.

a. Enthalpy of hydration of anhydrous or partially hydrated salts:

Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt.

For example, the hydration of anhydrous cupric sulphate is represented by

$CuSO_4\ (s) + 5H_2O\ (\ell) \rightarrow CuSO_4 . 5\ H_2O(s)$

There is almost invariably a liberation of heat in such reactions, i.e., the value of ΔH is negative.

$CuSO_4(s) + 800\ H_2O\ (\ell) \rightarrow CuSO_4\ 800\ H_2O$

$\Delta H_r° = -68\ kJ\ mol^{-1}$

$CuSO_4 . 5H_2O\ (s) + 795\ H_2O\ (\ell) \rightarrow CuSO_4\ 800\ H_2O$

$\Delta H_r° = +10\ kJ\ mol^{-1}$

by subtraction, we get $CuSO_4(s) + 5H_2O\ (\ell) \rightarrow$

$CuSO_4 . 5\ H_2O(s); \Delta H_r° = -78\ kJ\ mol^{-1}$

b. Enthalpy of hydration of gaseous ions.

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqueous ion.

By convention, the standard enthalpy of formation of $H^+(aq)$ is taken to be zero.

e.g., Enthalpy of hydration of Cl^- gaseous ions will be represented by:

$Cl^-(g) + aq. \rightarrow Cl^-(aq),\ \ \Delta H_r° = \Delta H_f°\ (Cl^-, aq)$

ENTHALPY OF DILUTION

The amount of heat evolved or absorbed when solution containing one mole of solute is diluted from one concentration to another. For example,

$HCl.10H_2O + 15H_2O \longrightarrow HCl.25H_2O$;

$\Delta H = -3.02\ kJ/mol$

This value of ΔH is the heat of dilution. The heat of dilution of a solution is dependent on the original concentration of the solution and on the amount of the solvent added.

ENTHALPY OF NEUTRALIZATION

- The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

or

- Enthalpy of neutralization is defined as the enthalpy change when one mole of H^+ in dilute solution combines with one mole of OH^- to give rise to undissociated water, i.e.,
  $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell);\ \Delta H = -57.1\ kJ/mole = -13.7\ kcal/mol$

Remember

- For Strong Acid + Strong Base, heat of neutralisation is always equal to –13.7 kcal/mole or –57.1 kJ/mole.
- For any other combination of acid and base this heat released is less than 13.7 kcal/mole or 57.1 kJ/mole.

ENTHALPY OF IONIZATION OF WEAK ELECTROLYTE

- Weak acids or weak bases are not completely ionized in solution. Some of the heat is consumed in ionizing these acids and bases. This heat is known as enthalpy of ionization and is defined per mole of the substance. Examples are:
  $HCN + Na^+OH^- \rightarrow Na^+ + CN^- + H_2O;\ \Delta_rH° = -12\ kJ\ mol^{-1}$
  $CH_3COOH + Na^+OH^- \rightarrow Na^+ + CH_3COO^- + H_2O;\ \Delta_rH° = -49\ kJ\ mol^{-1}$

The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,

Ionization $HCN \rightarrow H^+ + CN^-$; $\Delta H^\circ_1 = x$

Neutralization $H^+ + OH^- \rightarrow H_2O$; $\Delta H^\circ_2 = -57.1$ kJ/mole

The complete reaction is obtained by adding the above two steps. Thus

$HCN + OH^- \rightarrow H_2O + CN^-$

$\Delta H^\circ = -12$ kJ/mole

Obviously, $\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2$

$\Delta H^\circ_1 = \Delta H^\circ - \Delta H^\circ_2 = [-12 - (-57.1)] = 45.1$ kJ/mole

- Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.

ENTHALPY OF TRANSITION

Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.

For example: C(graphite) → C(diamond); $\Delta H_{trs}{}^0 = 1.90$ kJ mol^{-1}

Key Note

C(graphite) + $O_2(g) \rightarrow CO_2(g)$; $\Delta H_C{}^0 = -393.51$ kJ mol^{-1}

C(diamond) + $O_2(g) \rightarrow CO_2(g)$; $\Delta H_C{}^0 = -395.41$ kJ mol^{-1}

Subtracting, we have, C(graphite) → C(diamond)

$\Delta H_{trs}{}^0 = 1.90$ kJ mol^{-1}

ENTHALPY OF FORMATION OF IONS

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state as:

$(½)\ Cl_2(g) + aq \rightarrow Cl^-(aq)$; $\Delta H_f{}^\circ = \Delta H_f{}^\circ(Cl^-, aq)$

By convention, the standard enthalpy of formation of $H^+(aq)$ is taken to be zero.

Key Note

We have seen that

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$; $\Delta_r H^0 = -57.1$ kJ mol^{-1}

For this reaction, $\Delta H_r{}^0 = \Delta H_f{}^0(H_2O, l) - \{\Delta H_f{}^0(H^+, aq) + \Delta H_f{}^0(OH^-, aq)\}$

Hence, at 25°C, we get $\Delta H_f{}^0(H^+, aq) + \Delta H_f{}^0(OH^-, aq) = \Delta H_f{}^0(H_2O, l) - \Delta H_r{}^0$

so $\Delta H_f{}^0(OH^-, aq) = \{-286.1 - (-57.1)\}$ kJ mol^{-1}

$= -229.00$ kJ mol^{-1}

Enthalpy of Phase Change

(*a*) The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H^\circ$.

$H_2O(s) \rightarrow H_2O(l)$; $\Delta_{fus}H^\circ = 6.00$ kJ mol^{-1}

(*b*) Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap}H^\circ$.

$H_2O(l) \rightarrow H_2O(g)$; $\Delta_{vap}H^\circ = +40.79$ kJ mol^{-1}

(*c*) Standard enthalpy of sublimation, $\Delta_{sub}H^\circ$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).

Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or 'dry ice' sublimes at 195K with $\Delta_{sub}H^\circ = 25.2$ kJ mol^{-1}; naphthalene sublimes slowly and for this $\Delta_{sub}H^\circ = 73.0$ kJ mol^{-1}.

Enthalpy of Hydrogenation

The enthalpy change when one mole of given compound is hydrogenated.

e.g., $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$; $\Delta H^\circ = -30$ kcal/mol

Resonance Energy

It can be calculated as difference between enthalpy of formation (or combustion) (or hydrogenation) of actual molecule (i.e., resonance hybrid) & most stable resonating structure.

$$\Delta H^\circ_{resonance} = \Delta H^\circ_{f\,(experimental)} - \Delta H^\circ_{f\,(calculated)}$$

$$= \Delta H^\circ_{combustion\,(calculated)} - \Delta H^\circ_{combustion\,(experimental)}$$

Enthalpy of Atomisation

The enthalpy change when one mole of given compound is converted into gaseous atoms. e.g.,

$Na(s) \rightarrow Na(g)$

$CH_4(g) \rightarrow C(g) + 4H(g)$

Train Your Brain

Example 18: The enthalpies of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4.5H_2O$ are –66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$.

Sol. Given that

(*i*) $CuSO_4(s) + \text{aqueous} \longrightarrow CuSO_4(\text{aqueous})$;

$\Delta H_1 = -66.5$ kJ/mol

(*ii*) $CuSO_4.5H_2O(s) + \text{aqueous} \longrightarrow CuSO_4(\text{aqueous})$;

$\Delta H_2 = 11.7$ kJ/mol

$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s)$;

$\Delta H = ?$

$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - 11.7 = -78.2$ kJ

Example 19: 150 ml of 0.5 N nitric acid solution at 25.35°C was mixed with 150 ml of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77°C. Calculate the heat of neutralisation of nitric acid with sodium hydroxide.

Sol. Total mass of solution = 150 + 150 = 300 gm

$Q = 300 \times (28.77 - 25.35) = 300 \times 3.42 = 1026$ cal

$$\therefore \text{ Heat of neutralisation} = \frac{Q}{150}\times 1000\times\frac{1}{0.5}$$

$$= \frac{1026}{150}\times 1000\times\frac{1}{0.5} = 13.68 \text{ kcal.}$$

Since, the enthalpy of neutralisation is always –ve, so, heat of neutralisation = – 13.68 kcal.

Example 20: Calculate the enthalpy change when one mole of HCl(g) is dissolved in a very large amount of water at 25°C. The change in state is:

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$$

Given: $\Delta_f H°(HCl, g) = -92 \text{ kJ mol}^{-1}$ and

$\Delta_f H° (Cl^-, aq) = -167 \text{ kJ mol}^{-1}$

Sol. For the reaction,

$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$

we have $\Delta H° = \Delta H°(Cl^-, aq) - \Delta_f H°(HCl, g)$

$\Delta H° = [-167 - (-92)] \text{ kJ mol}^{-1} = -75 \text{ kJ mol}^{-1}$

Example 21: Calculate ΔH° for the reaction,

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

at 25°C. Given $\Delta_f H° (Ag^+, aq) = 105 \text{ kJ mol}^{-1}$, $\Delta_f H° (Cl^-, aq) = -167 \text{ kJ mol}^{-1}$ and $\Delta_f H°(AgCl, s) = -127 \text{ kJ mol}^{-1}$

Sol. For the reaction $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

we have

$\Delta H° = \Delta_f H° (AgCl, s) - \Delta_f H°(Ag^+, aq) - \Delta_f H°(Cl^-, aq)$

$= [-127 - 105 - (-167)] \text{ kJ mol}^{-1}$

$= -65 \text{ kJ mol}^{-1}$

Example 22: Enthalpy of neutralization of HCl by NaOH is –57.1 kJ/mol and by NH_4OH is –51.1 kJ/mol. Calculate the enthalpy of dissociation of NH_4OH.

Sol. Given that

$H^+(aq) + NH_4OH(aq) \rightarrow NH_4^+(aq) + H_2O(\ell)$

$\Delta H = -51.1$ kJ/mole

We may consider neutralization in two steps.

(*i*) Ionization

$NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-(aq)$

$\Delta H_1 = ?$

(*ii*) Neutralization

$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

$\Delta H_2 = -57.1$ kJ/mole

Thus, $\Delta H = \Delta H_1 + \Delta H_2$

Therefore,

$\Delta H_1 = \Delta H - \Delta H_2 = -51.1 \text{ kJ/mol} + 57.1 \text{ kJ mol}^{-1}$

$= 6.0$ kJ/mol

Concept Application

19. 10 mL of each 1 M HCl and 1M H_2SO_4 are neutralized by 1 M NaOH solution that liberate the heat of a & b kJ/mol respectively. What is relation between a and b?

(*a*) a = b (*b*) a = 2b
(*c*) 2a = b (*d*) a = 4b

20. The standard enthalpy of neutralization of KOH with HCN and HCl in dilute solution is –2480 cal.mol^{-1} and –13.68 kcalmol^{-1} respectively. Find the enthalpy of dissociation of HCN at the same temperature.

(*a*) 5.2 kcal (*b*) 11.2 kcal
(*c*) 15 kcal (*d*) 22.4 kcal

21. The neutralisation of a strong acid by a strong base liberates an amount of energy per mole of H^+ that-

(*a*) Depends upon which acid and base are involved.
(*b*) Depends upon the temperature at which the reaction takes place.
(*c*) Depends upon which catalyst is used.
(*d*) Is always the same

22. Find heat of reaction for the given acid-base reaction,

$HA + NaOH \rightarrow NaA + H_2O$; $\Delta H = -4.7$ kcal/mol

the heat of dissociation of HA :

(*a*) 9 kcal/mol (*b*) –18.4 kcal/mol
(*c*) +18.4 kcal/mol (*d*) –9 kcal/mol

BOND ENTHALPIES

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While **bond dissociation enthalpy** is the enthalpy required to dissociate a given bond of some specific compound.for example the enthalpy of dissociation of the O–H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.

$H_2O(g) \rightarrow H(g) + OH(g)$ $\Delta H_r^0 = 501.87 \text{ kJ mol}^{-1}$

However, to break the O–H bond in the hydroxyl radical required a different quantity of heat:

$OH(g) \rightarrow O(g) + H(g)$ $\Delta H_r^0 = 423.38 \text{ kJ mol}^{-1}$

The bond enthalpy, ΔH_{OH}, is defined as the average of these two values, that is:

$$\Delta H_{OH} = \frac{501.87 \text{kJmol}^{-1} + 423.38 \text{kJmol}^{-1}}{2}$$

$$= 462.625 \text{ kJ mol}^{-1}$$

In the case of diatomic molecules, such as H_2, the bond enthalpy and bond dissociation enthalpy are identical.

Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthalpies of the bond for a number of molecules in which the pair of atoms appears.

- **Estimation of Enthalpy of a reaction from bond Enthalpies:** Let the enthalpy change for the gaseous reaction

$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$

be required from the bond enthalpy data. This may be calculated as follows:

$$\Delta H = \left(\begin{array}{l}\textit{Enthalpy} \text{ required to break reactants} \\ \text{into gaseous atoms}\end{array}\right) - \left(\begin{array}{l}\textit{Enthalpy} \text{ required to break products} \\ \text{into gaseous atoms}\end{array}\right)$$

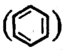
$$= [4\Delta H_{C-H}+\Delta H_{C=C}+\Delta H_{H-Cl}] + [-5\Delta H_{C-H}-\Delta H_{C-C}-\Delta H_{C-Cl}]$$

$$= (\Delta H_{C=C} + \Delta H_{H-Cl}) - (\Delta H_{C-H} + \Delta H_{C-C} + \Delta H_{C-Cl})$$

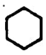
Train Your Brain

Example 23: The standard molar enthalpies of formation of cyclohexane (ℓ) and benzene (ℓ) at 25°C are −156 and + 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (ℓ) at 25° is −119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene.

Sol. Enthalpy of hydrogenation of 3 carbon-carbon double bonds

$= \Delta H_F$ ( ) $- \Delta H_f$ ()

$= -156 - (+49)$ kJ $= -205$ kJ/mol

Given that, $+ H_2 \longrightarrow$  $\Delta H = 119$ kJ/mol

Theoretical enthalpy of hydrogenation of 3 double bonds in benzene ring

$= 3 \times (-119)$ kJ $= -357$ kJ/mol

∴ Resonance energy of benzene

$= -357 - (-205)$ kJ $= -152$ kJ mole^{-1}

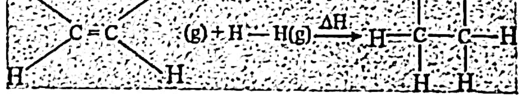
Example 24: Using the bond enthalpy data given below, calculate the enthalpy change for the reaction

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Data :

Bond	Bond enthalpy
C − C	336 kJ mol^{-1}
C = C	606 kJ mol^{-1}
C − H	410 kJ mol^{-1}
H − H	431 kJ mol^{-1}

Sol. Diagrammatically, we represent the given reaction as follows:



$\Delta H_{reaction} = \Sigma(B.E)_{reactant} - \Sigma(B.E.)_{product}$

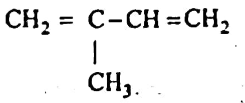
$= [4 \text{ B.E. } (C-H)] + \text{B.E. } (C=C) + \text{B.E}(H-H)]$

$- [6 \text{ B.E. } (C-H) + \text{B.E.}(C-C)]$

$= [4 \times 410 + 606 + 431] - [6 \times 410 + 336]$

$= -119$ kJ/mol.

Example 25: Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



$$\underset{\displaystyle CH_3}{CH_2 = \overset{}{C}} - CH = CH_2$$

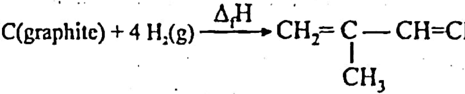
Data: Bond enthalpy of C − H bond = 413.38 kJ mol^{-1}

Bond enthalpy of C − C bond = 347.69 kJ mol^{-1}

Bond enthalpy of C = C bond = 615.05 kJ mol^{-1}

Enthalpy of sublimation of carbon (graphite) = 718.39 kJ mol^{-1}

Enthalpy of dissociation of $H_2(g)$ = 435.97 kJ mol^{-1}

Sol. 

$$5C(\text{graphite}) + 4\,H_2(g) \xrightarrow{\Delta_f H} CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH = CH_2$$

$\Delta_f H = (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 - 8 \times 413.38)$ kJmol^{-1} $= 103.31$ kJ mol^{-1}

Concept Application

23. Estimate the average S–F bond enthalpy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, S(g) and F(g) are: −1100, 274 and 80 kJ mol^{-1} respectively.

(*a*) −746 kJ mol^{-1} (*b*) 309 kJ mol^{-1}

(*c*) 618 kJ mol^{-1} (*d*) 154.5 kJ mol^{-1}

24. Calculate the enthalpy change (ΔH) of the following reaction:

$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$ given average bond enthalpies of various bonds, i.e., C–H, C≡C, O = O, C = O, O–H as 414, 814, 499, 724 and 640 kJ mol^{-1} respectively.

(*a*) −2573 kJ mol^{-1} (*b*) + 2573 kJ mol^{-1}

(*c*) −1286.5 kJ mol^{-1} (*d*) 1087 kJ mol^{-1}

25. Bond energies of N ≡ N; H − H and N − H bonds are 945, 463 & 391 kJ mol^{-1} respectively, the enthalpy change of the following reaction is:

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(*a*) +93 kJ/mol (*b*) −93 kJ/mol

(*c*) −46.5 kJ/mol (*d*) +46 kJ/mol

26. Enthalpy change of the reaction $2H(g) \rightarrow H_2(g)$ is - 104 Kcal The H − H bond dissociation energy is:

(*a*) 104 kcal/mol (*b*) −104 kcal/mol

(*c*) −52 kcal/mol (*d*) +52 kcal/mol

27. For the equations

C(diamond) + $2H_2(g) \rightarrow CH_4(g)$; ΔH_1

$C(g) + 4H(g) \rightarrow CH_4(g)$; ΔH_2

Predict whether

(*a*) $\Delta H_1 = \Delta H_2$ (*b*) $\Delta H_1 > \Delta H_2$

(*c*) $\Delta H_1 < \Delta H_2$

(*d*) $\Delta H_1 = \Delta H_2 + \Delta_{vap}H(C) + \Delta_{diss}H(H_2)$

Importance of Second Law

What is the driving force for a process which takes system from one state to other on its own? Why such processes (called spontaneous process) take place at all? Answers to these questions are given by second law.

SPONTANEOUS PROCESS

A spontaneous process is the one which takes place on its own & can drive some other process as well. However, in some cases, initiation may be required.

Example:

(*i*) Mixing of two gases.

(*ii*) Cooling of a hot object by transferring heat to surrounding.

(*iii*) Water flowing down the hill.

(*iv*) Rusting of iron.

(*v*) Burning of coal, coke, hydrocarbons.

(*vi*) Volcanic eruptions.

The synonyms of spontaneous processes are **natural processes** and irreversible processes.

It is a common observation that natural processes occur with finite rate. All spontaneous processes take place due to a finite driving force (which can be temperature difference, height difference, potential energy difference, etc.). Also the change brought about by a spontaneous process can not be restored without making some effort (which brings about permanent change in surrounding). Hence it is quite natural to call these processes as irreversible processes.

DISORDER

The term 'disorder' is related to randomness. Any macroscopic property of a system is an average of large number of microscopic forces which are random in nature. Greater the randomness associated with microscopic forces, greater is the uncertainty about exact microscopic description of a macroscopic state and greater will be the disorder associated with the macroscopic state.

As a rule:

(*i*) Greater the number of molecules in which a given energy is distributed, greater is the disorder.

(*ii*) Greater the spread of given number of molecules with given energy in space, greater will be the disorder.

SECOND LAW OF THERMODYNAMICS

For any spontaneous process (irreversible process):

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

During a reversible process:

$$\Delta S_{\text{universe}} = 0$$

Thus during irreversible process, entropy of universe increases while during reversible process, entropy of universe remains constant.

Entropy

Entropy is a measure of disorder. The entropy is a state function and a basic quantity directly defined by second law.

There are three types of entropy changes:

(*i*) ΔS_{system} : Entropy change of system

(*ii*) $\Delta S_{\text{Surrounding}}$: Entropy change of surrounding

(*iii*) $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = \Delta S_{\text{universe}} = \Delta S_{\text{total}} = \Delta S_{\text{isolated}}$

The change in entropy of a system is given by:

$dS = \dfrac{dq_{rev}}{T}$ where; dq_{rev} = heat exchanged by system in a very small step (reversibly).

Key Note

Physical Significance of Quantity $\dfrac{dq_{rev}}{T}$

T = absolute temperature at which heat is absorbed.

Suppose, similar quantity of heat is absorbed at two different temperatures T_1 and T_2 ($T_2 >> T_1$). When heat is supplied at high temperature, the % increase in kinetic energy is less compared to heat supplied at low temperature. Hence, **disorder will increase by greater value, when heat is supplied at lower temperature.**

ENTROPY CHANGE OF AN IDEAL GAS

From definition of entropy of system

$$dS_{\text{system}} = \frac{dq_{rev}}{T} \quad \text{... (i)}$$

From first law, $dq_{rev} = dU + PdV$

For a reversible change involving an ideal gas

$$dq_{rev} = nC_{V.m}.dT + \frac{n_{RT}}{V}.dV \quad \text{... (ii)}$$

$$\Rightarrow \int_1^2 \frac{dq_{rev}}{T} = \int_1^2 \frac{nC_{v.m}dT}{T} + \int_{V_1}^{V_2} nR\frac{dV}{V}$$

$$\Delta S_{\text{system}} = nC_{v.m}\ln\frac{T_2}{T_1} + nR\ln\left(\frac{V_2}{V_1}\right) = nC_{p.m}\ln\frac{T_2}{T_1} - nR.\ln\frac{P_2}{P_1}$$

This formula is applicable to all ideal gas process.

Ideal Gas Processes

(i) For isothermal change

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T} = \frac{1}{T}\int_1^2 dq_{rev} \qquad (\because T = \text{constant})$$

$$\Rightarrow \Delta S = \frac{q_{rev}}{T} = nR\ell n\left(\frac{V_2}{V_1}\right) \qquad \left[\because q_{rev} = nRT\ln\left(\frac{V_2}{V_1}\right)\right]$$

(ii) For isochoric change

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_1^2 \frac{nC_{v.m}dT}{T} = nC_{vm}\int_1^2 \frac{dT}{T} \qquad (\because dq_v = nC_{V.m}.dT)$$

$$\Rightarrow \Delta S = nC_{V.m}\,\ell n\frac{T_2}{T_1}$$

(iii) For isobaric change

$$\Delta S = \int \frac{dq_P}{T} = \int_1^2 \frac{nC_{P.m}.dT}{T} = nC_{P.m}\int_1^2 \frac{dT}{T} \qquad (\because dq_P = nC_{P.m}.dT)$$

$$\Rightarrow \Delta S = nC_{P.m}\,\ell n\frac{T_2}{T_1}$$

(iv) Reversible adiabatic process

$$\Rightarrow \Delta S = \underbrace{nC_v \ln \frac{T_2}{T_1}}_{\text{entropy changed due to change in temperature}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{entropy changed to change in volume}}$$

(a) During reversible adiabatic expansion:

$T_2 < T_1$ and $V_2 > V_1$

$\Rightarrow$ Sign of two terms are opposite and magnitudes are same because for reversible adiabatic process –

$$nC_{V,m} \ln \frac{T_2}{T_1} = -nR \ln \left(\frac{V_2}{V_1}\right)$$

$\Rightarrow$ +ive and –ive term cancel out each other and hence, $\Delta S = 0$

Thus, decrease in entropy during expansion due to decrease in temperature is exactly cancelled out by increase in entropy due to increase in volume of system in reversible adiabatic expansion.

(b) During reversible adiabatic compression:

$T_2 > T_1$ and $V_2 < V_1$

$$\Delta S_{Total} = \underbrace{nC_v \ln \frac{T_2}{T_1}}_{+\text{ive}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{-\text{ive}}$$

Thus, increase in entropy due to increase in temperature is compensated by decrease in entropy due to decrease in volume of system in reversible adiabatic compression. Hence. $\Delta S = 0$ for reversible adiabatic compression.

(v) Irreversible adiabatic process

Since process is irreversible, $\Delta S_{Total} > 0$.

$\because \Delta S_{surr} = 0$

The physical interpretation is -

(a) During irreversible adiabatic compression, large quantity of heat is produced while decrease is volume is less. Thus increase in entropy due to rise in temperature exceeds the decrease in entropy due to decrease in volume. Hence net entropy change is positive.

(b) During irreversible adiabatic expansion, due to sudden decrease in external pressure, the system remains less challenged during expansion. Hence system do less work-resulting in lesser decrease in temperature. The increase in volume of system is relatively larger.

Thus increase in entropy due to increase in volume exceeds decrease in entropy due to decrease in temperature. The net change in entropy is positive in both processes $\Delta S_{surr} = 0$ ($\because$ no heat is exchanged with surrounding) and $\Delta S_{total} > 0$.

(vi) Free expansion of an ideal gas against vacuum

Free expansion of an ideal gas is an example of irreversible adiabatic as well as irreversible isothermal process.

During free expansion, the $P_{ext} = 0$. Hence, the ideal gas is not challenged at all during expansion. The kinetic energy of ideal gas remains constant. Hence, no temperature difference is created during expansion between system and surrounding.

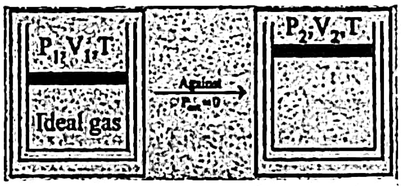
$\because \Delta T = 0$, the heat absorbed during the process = 0

Since $V_f > V_i$ and T = constant, $\Delta S_{system} > 0$

The free expansion is an example where $q_{actual} = 0$, still $\Delta S_{system} > 0$.

This is reasonable, because: $\Delta S_{system} = \int \frac{dq_{rev}}{T}$.

This, example clearly shows that even if q_{actual} between two states is zero, this does not means that $\int_1^2 \frac{dq_{rev}}{T}$ between two states is zero. This outlines the importance of reversible path and $q_{rev.}$ in calculation of entropy of system.



$q_{irr} = 0$; $w_{irr} = 0$

$$\Delta S_{system} = \int_1^2 \frac{dq_{rev}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{surr} = \frac{-q_{irr}}{T} = 0 \Rightarrow \Delta S_{total} = nR \ln \left(\frac{V_2}{V_1}\right) > 0$$

Entropy Calculation

Process	ΔS_{sys}	ΔS_{surr}
Isothermal reversible	$nR \ln \left(\frac{V_2}{V_1}\right)$	$-nR \ln \left(\frac{V_2}{V_1}\right)$
Isothermal irreversible	$\Delta S_{sys} = nR\,ln \left(\frac{V_2}{V_1}\right)$	$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{W_{sys}}{T} = \frac{-P_{ext}(V_2 - V_1)}{T}$
Adiabatic reversible	$\Delta S_{sys} = 0$	$\Delta S_{surr} = 0$
Adiabatic irreversible	$\Delta S_{sys} = nC_{v,m}\,ln \frac{T_2}{T_1} + nR\,ln \left(\frac{V_2}{V_1}\right)$	$\Delta S_{surr} = 0$

Isobaric reversible	$\Delta S_{sys} = nC_{p,m} \ln \frac{T_2}{T_1}$	$\Delta S_{surr} = -\Delta S_{sys}$
Isochoric reversible	$\Delta S_{sys} = nC_{V,m} \ln \frac{T_2}{T_1}$	$\Delta S_{surr} = -\Delta S_{sys}$

Entropy Change of Solids and Liquids Upon Heating

$\Delta s = \int \frac{dq_{rev}}{T} = \int \frac{ms\,dT}{T} = ms\,\ell n \frac{T_2}{T_1}$ [s = specific heat of solid/liquid].

For molar change in entropy, m = M(g/mole); where M = molar mass.

Key Note

- For solids and liquids ($Ms \cong C_p \cong C_v$).

Reversible Phase Transitions

Reversible phase transition are always isothermal & isobaric.

$$\Delta S_{system,\,P,T} = \frac{q_{rev}}{T} = \frac{\Delta H_{P,T}}{T_{Transition}}$$

$$\Delta S_{surr} = \frac{-\Delta H_{P,T}}{T_{Transition}}$$

$$\Delta S_{total} = 0$$

Thus $\Delta S_{vaporisation}$ at boiling point = $\frac{\Delta H_{vaporisation}}{T_{vaporisation}}$

ΔS_{fusion} at melting point = $\frac{\Delta H_{fusion}}{T_{fusion}}$

$\Delta S_{sublimation}$ at sublimation point = $\frac{\Delta H_{sublimation}}{T_{sublimation}}$

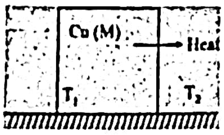
$$\Delta S_{allotropic\ modification} = \frac{\Delta H_{allotropic\ modification}}{T_{transition}}$$

Entropy Calculation for Solid or Liquid Systems

(*a*) 'Cu' block kept in open atmosphere

$$\Delta S_{system} = \int_{T_1}^{T_2} \frac{ms\,dT}{T} = ms\ \ln \frac{T_2}{T_1}$$

$$\therefore\ \Delta S_{surr} = \int \frac{dq_{surr}}{T} = \frac{q_{surr}}{T_2}$$



$T_1 > T_2$

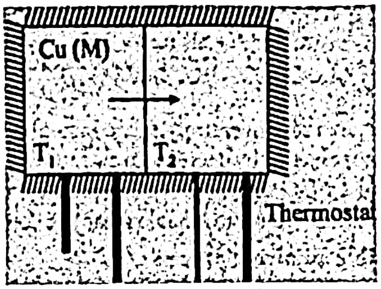
but $q_{surr} = -q_{system} = -ms\,(T_2 - T_1) = ms\,(T_1 - T_2)$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

$$\therefore\ \Delta S_{universe} = ms\ \ell n\ \frac{T_2}{T_1} + \frac{ms\,(T_1 - T_2)}{T_2} > 0$$

(*b*) Two copper block kept in contact in thermostat

Two blocks are of same mass



$\Delta S_{surr} = 0$ (since no heat is lost to surrounding)

$\Delta S_{system} = \Delta S_A + \Delta S_B$

System will reach a common temperature (T_f) and $T_1 > T_f > T_2$

$$\Delta S_{system} = \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T}$$

$$= \int_{T_1}^{T_f} \frac{ms\,dT}{T} + \int_{T_2}^{T_f} \frac{ms\,dT}{T} = ms\left[\ell n \frac{T_f}{T_1} + \ell n \frac{T_f}{T_2}\right]$$

$$\Delta S_{system} = ms\,\ell n \frac{T_f^2}{T_1 T_2}$$

Since $T_f = \frac{T_1 + T_2}{2}$

$$\therefore\ \Delta S_{system} = ms\,\ell n \frac{(T_1 + T_2)^2}{4T_1T_2}$$

Key Note

- Spontaneity of a process in terms of total entropy change
  If, $\Delta S_{total} = +ve \Rightarrow$ spontaneous process
  If, $\Delta S_{total} = -ve \Rightarrow$ non spontaneous process
  If, $\Delta S_{total} = 0 \Rightarrow$ process is at equilibrium

Credit:--- Divansh.....

Train Your Brain

Example 26: What are the signs of ΔS for the system and for the surrounding in each of the following processes?

(*a*) Water boils in a tea kettle on a hot stove.

(*b*) Ice in an ice cube tray left on a table melts.

(*c*) A cup of coffee is reheated in a microwave oven.

Sol. (*a*) ΔS_{sys} is positive ; ΔS_{surr} is negative.

(*b*) ΔS_{sys} is positive, ΔS_{surr} is negative.

(*c*) ΔS_{sys} is positive, ΔS_{surr} is negative.

Example 27: State the thermodynamic condition of spontaneous occurance of a process?

Sol. $\Delta G = (-)$ ve or $\Delta S_{total} > 0$

Example 28: The entropy of vaporization of benzene is $85\ JK^{-1}\ mol^{-1}$. When 117 g benzene vaporizes at it's normal boiling point, calculate the entropy change of surrounding.

Sol. 1.5×85 J/K

Example 29: Three moles of an ideal gas is expanded isothermally from 2L to 10L, at 27°C. Calculate ΔS_{sys} and ΔS_{surr} and ΔS_{univ} if the process is performed.

(*i*) Reversibly

(*ii*) Irreversibly, against a constant external pressure of 1 atm.

(*iii*) As free expansion.

Sol. (*i*) $\Delta S_{univ} = 0$, $\Delta S_{surr} = -\Delta S_{sys}$

and $\Delta S_{sys} = nR\,ln\left(\frac{V_2}{V_1}\right) = 3R\,ln\,\frac{10}{2} = 40.14$ J/K

(*ii*) $\Delta S_{sys} = 40.14$ J/K

$$\Delta S_{surr.} = \frac{P_{ext.}(V_2 - V_1)}{T} = \frac{1 \times (10-2) \times 101.3}{300}$$

$= -2.7$ J/K

and $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 37.44$ J/K

(*iii*) $\Delta S_{sys} = 40.14$ J/K

$\Delta S_{surr} = 0$ as $P_{ext} = 0$

and $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 40.14$ J/K

Concept Application

28. One mole of an ideal diatomic gas ($C_v = 5$ cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. The entropy change of the process can be expressed as:
(R = 2 calories/mol/K)

(*a*) $3\ln\frac{298}{373} + 2\ln 10$ (*b*) $5\ln\frac{373}{298} + 2\ln 10$

(*c*) $7\ln\frac{373}{298} + 2\ln\frac{1}{10}$ (*d*) $5\ln\frac{373}{298} + 2\ln\frac{1}{10}$

29. Calculate the entropy change in surroundings when 1.00 mol of $H_2O\ (l)$ is formed under standard conditions at 298 K. Given $\Delta_f H^\circ = -286\ kJ\ mol^{-1}$.

(*a*) 959.73 JK^{-1} (*b*) −959.73 JK^{-1}

(*c*) 766.75 JK^{-1} (*d*) −766.75 JK^{-1}

30. If one mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ is expanded isothermally at 300 K until it's volume is tripled, then change in entropy of gas is:

(*a*) zero (*b*) Infinity

(*c*) $\frac{5}{2}R\ln 3$ (*d*) $R\ln 3$

THIRD LAW OF THERMODYNAMICS

"At absolute zero, the entropy of a perfectly crystalline substance is zero", which means that at absolute zero, every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_{T(K)} - S_{0(K)} = \int_0^T \frac{q_{rev}}{T}$$

Since $S_{0(K)} = 0$

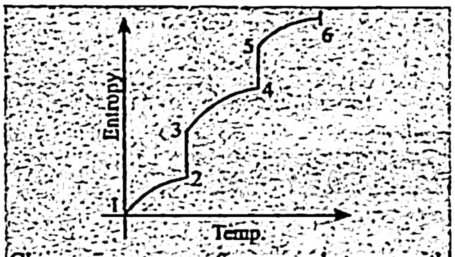
$$S_T = \int_0^T \frac{q_{rev}}{T}$$

The variation of entropy of a substance with temperature is given by graph:

At 1, entropy of substance is zero.

- from 1-2; The temperature of solid increases upon heating -

$$\Rightarrow S_2 - S_1 = \int \frac{C_{P,solid}}{T} dT \qquad \text{—(i)}$$



Change in entropy of a pure substance with temperature at constant pressure.

- from 2-3; The temperature remains constant during phase transition

$$\Rightarrow S_3 - S_2 = \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f} \qquad \text{—(ii)}$$

- from 3-4; The temperature of liquid increases

$$\Rightarrow S_4 - S_3 = \int_{T_3}^{T_4} \frac{C_{P,liquid}.dT}{T} \quad ...(iii)$$

- ◆ from 4-5; Reversible vaporisation takes place at constant temperature:

$$\Rightarrow S_5 - S_4 = \Delta S_{vap.} = \frac{\Delta H_{vap}}{T_b} \quad ...(iv)$$

- ◆ from 5-6; The gas is heated

$$\Rightarrow S_6 - S_5 = \int_{T_5}^{T_6} \frac{C_{P,gas}.dT}{T} \quad ...(v)$$

$$\Delta S_{1-6} = (S_2 - S_1) - (S_3 - S_2) - (S_4 - S_3) - (S_5 - S_4) - (S_6 - S_1)$$
$$= (S_6 - S_1)$$
$$[\because S_1 = 0]$$

- ◆ from 5-6; absolute entropy at 6 =

$$\int_{T_1}^{T_f} \frac{C_{P,solid}dT}{T} + \frac{\Delta H_{fusion}}{T_f} + \int_{T_f}^{T_b} \frac{C_{P,liquid}dT}{T} + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{C_{P,gas}dT}{T}$$

Standard Absolute Molar Entropy

It is the entropy of one mole of substance at standard temperature at 1 bar.

It is calculated assuming that substance is heated isobarically and reversibly at 1 bar from 0 K to standard temperature.

Comparing Absolute Entropies of Substance

(*i*) The absolute entropies of substance follow the order,

$$S(g) >> S(l) > S(s)$$

(*ii*) Entropy increases when solid and liquid is dissolved into solvent,

e.g. $CH_3OH(l)$ S° = 127 J/K-mole
$CH_3OH(aq)$ S° = 132.3 J/K-mole
$NaCl(s)$ S° = 72.4 J/K-mole
$NaCl(aq.)$ S° = 115.4 J/K-mole

(*iii*) The entropy of dissolved gas is less than pure gas.

e.g. $HCl(g)$ S° = 186.7 J/K-mole
$HCl(aq)$ S° = 55.2 J/K-mole

(*iv*) Entropy rises with increasing molar mass, (if other factors are similar).

e.g. $F_2(g)$ S° = 203 J/K-mole
$Cl_2(g)$ S° = 223 J/K-mole
$Br_2(g)$ S° = 245 J/K-mole

(*v*) Entropy is lower in covalently bonded solids, with strong directional bonds, than in solids with partial metallic character.

e.g. C(diamond) S° = 2.44 J/K-mole
C(graphite) S° = 5.69 J/K-mole
Sn(gray) S° = 44.8 J/K-mole
Sn(white) S° = 51.5 J/K-mole

(*vi*) Entropy increases with increasing softness and with weakness of bonds between atoms.

e.g.	C(diamond)	Be(s)	$SiO_2(s)$	Pb(s)	Hg(*l*)
	2.44	9.54	41.8	64.9	77.4
	diamond	hard metal	quartz	soft metal	liquid

(*vii*) Entropy increases with chemical complexity.

NaCl	$MgCl_2$	$AlCl_3$
72.4	89.5	167

For $CuSO_4.nH_2O$

n = 0,	n = 1,	n = 3,	n = 5
S° = 113,	150	225,	305

Entropy Change (ΔS) of a Chemical Reaction

The change in entropy when reactants turn into products according to a balanced chemical reaction with specified physical state of each reactant and product is called entropy change of reaction.

- ◆ **Consider a reaction:**

$$aA(m) + bB(n) \xrightarrow{T.P} cC(o) + dD(p)$$

where m, n, o and p are physical states at temperature T and pressure P.

$\Delta S = \sum S$ (products) – $\sum S$ (reactants)

$$\Delta_r S = cS_c + dS_D - aS_A - bS_B$$

S_A, S_B, S_C and S_D are absolute molar entropies at temperature T and pressure P **(from third law)**

So, $\Delta_r S$ is evaluated from table of data of third law entropies of various substances.

Train Your Brain

Example 30: Predict which of the following reaction(s) have a positive entropy change?

I. $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$
II. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
III. $2SO_3(g) \longrightarrow 2SO_2(g) + O_2(g)$

Sol. (II and III)
Δn_g value for (I = 0) for (II,III = 1)
Δn_g is + ve for II,III

Concept Application

31. Identify the correct statement regarding a spontaneous process:

(*a*) For a spontaneous process in an isolated system, the change in entropy is positive.
(*b*) Endothermic processes are never spontaneous.
(*c*) Exothermic processes are always spontaneous.
(*d*) Lowering of energy in the reaction process is the only criterion for spontaneity.

Credit:--- Divansh.....

32. ΔS for the reaction ; $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ will be:

(*a*) 0 (*b*) –ve

(*c*) +ve (*d*) ∞

33. Change in entropy is negative for:

(*a*) Bromine (*l*) → Bromine (g)

(*b*) $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

(*c*) N_2(g, 10 atm. 298 K) → N_2 (g, 1 atm. 298K)

(*d*) Fe(at 400 K) → Fe (at 300 K)

34. For which reaction from the following, ΔS will be maximum?

(*a*) $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$

(*b*) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(*c*) $C(s) + O_2(g) \rightarrow CO_2(g)$

(*d*) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

35. For the process, $CO_2(s) \rightarrow CO_2(g)$:

(*a*) Both ΔH and ΔS are +ve.

(*b*) ΔH is –ve and ΔS is +ve.

(*c*) ΔH is +ve and ΔS is –ve.

(*d*) Both ΔH and ΔS are –ve.

GIBB'S FREE ENERGY

Gibb's free energy 'G' is defined as G = H – TS.

it is a state function and is an extensive property.

Gibb's free energy provide a very useful criteria for spontanity of a process taking place at constant temperature and pressure (isobaric, isothermal process).

The entropy of universe is also a very useful criteria of spontanity, but it is based on properties of system as well as surrounding.

The Gibb's free energy provides criteria for spontaneity based only on the properties of system.

$\Delta G = \Delta H - \Delta(TS)$;

$\Delta G = \Delta H - T\Delta S$ (at constant temperature)

$\Delta G_{T,P}$ and $\Delta S_{universe}$

Decrease in Gibb's free energy at constant temperature and pressure is related to ΔS_{total} (total entropy change of system and surrounding).

$-\Delta G = T(\Delta S_{total})$

At constant P, T

if ΔG < 0 ⇒ spontaneous process.

if ΔG > 0 ⇒ non-spontaneous process.

if ΔG = 0 ⇒ reversible process.

Calculate ΔG for Various Processes

(*i*) **Ideal gas subjected to isothermal compression or expansion:**

For isothermal change:

$\Delta G = \Delta H - T\Delta S$

For ideal gas, $\Delta H = nC_{Pm}\Delta T = 0$

(As ΔT = 0, for isothermal change)

$\& \ \Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$ (for isothermal change)

$\Delta G = -nRT \ln\left(\frac{V_2}{V_1}\right)$

Hence, during isothermal expansion Gibb's free energy decreases while during isothermal compression Gibb's function increases.

(*ii*) **Isothermal and isobaric phase transitions:**

At transition temperature, the stability (or Gibb's free energy) of two phases are equal. Hence, there is no driving force for conversion of one phase into other. This means phase transitions are examples of reversible processes at transition temperature.

Now, for reversible isothermal and isobaric change, ΔG = 0

⇒ ΔG = 0, for phase transitions at transition temperature.

Thus, ΔG = 0 at boiling point.

Also, $\Delta G_{vap} = 0$ at melting point:

$\Delta H_{fusion} = T_{fusion}\Delta S_{fusion}$

$T_{fusion} = \frac{\Delta H_{fusion}}{\Delta S_{fusion}}$

(*iii*) **$\Delta_r G$ for a chemical reaction.**

Consider a reaction : $aA + bB \xrightarrow{T,P} cC + dD$

The change in Gibb's free energy for a chemical reaction is change in ΔG when reactants react according to a given balanced chemical reaction with specified physical state of each reactant and product at given temperature and pressure.

$\Delta_r G = cG_c + dG_D - aG_A - bG_B$ —(i)

Where G_A, G_B, G_C and G_D are molar Gibb's free energy of A, B, C and D respectively at given T and P. also,

$$\left.\begin{matrix} G_A = H_A - TS_A \\ G_B = H_B - TS_B \\ G_C = H_C - TS_C \\ G_D = H_D - TS_D \end{matrix}\right\} \quad \text{—(ii)}$$

Substituting (ii) in (i)

$\Delta_r G = (cH_c + dH_D - aH_A - bH_B) - T(cS_c + dS_D - aS_A - bS_B)$

$\Rightarrow \Delta_r G = \Delta_r H - T\Delta_r S$

$(\Delta H_r)_{T,P}$	$(\Delta S_r)_{T,P}$	(ΔG_r)	Remarks
– ve	+ ve	Always -ve	Reaction is spontaneous
+ ve	– ve	Always +ve	Reaction non-spontaneous
+ ve	+ ve	At low temperature, AG = + ve At high temperature, AG = – ve	Non-spontaneous Spontaneous
– ve	– ve	At low temperature. ΔG = – ve At high temperature, ΔG = + ve	Spontaneous Non spontaneous

(iv) Gibb's energy functions of pure substances:

Consider a pure substance having a Gibb's energy function as follows:

$G = H - TS = U + PV - TS$

Let, the pressure and temperature are varied by infinitesimally small value:

$dG = dU + PdV + VdP - TdS - SdT$

As, $dU = dq - PdV$ and $TdS = dq$ [Assume only PV- work and reversible process.]

$\mathbf{dG = VdP - SdT}$

(a) If pressure is varied keeping temperature constant -

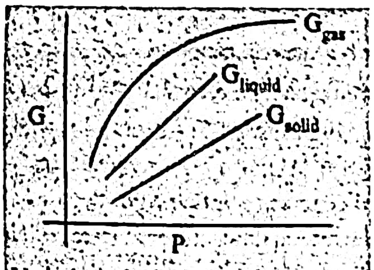
$$dG = VdP \Rightarrow \left(\frac{dG}{dP}\right)_T = V$$

The physical significance of above relation is when pressure over a substance is increased, it's Gibb's function increases & the increase is proportional to molar volume. Since molar volume of gas, liquid and solid are in order, as follows:

$V_{Gas} > V_{Liquid} > V_{Solid}$

Hence, Gibb's function of gases increases most rapidly on increasing pressure.

That's why, gas phase becomes unstable at high pressure.



Variation of Gibb's function of pure substance with pressure at constant temperature

(b) If temperature is changed keeping pressure constant

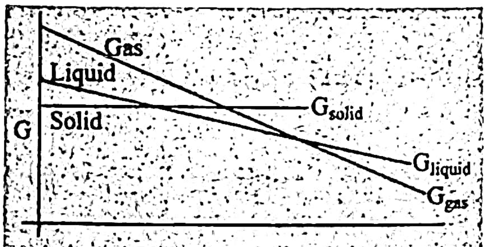
$$dG = -SdT \Rightarrow \left(\frac{dG}{dT}\right)_P = -S$$

Since entropy of pure substances are always positive, the slope of G vs T curve is negative. Also since,

$S_{gas} > S_{liquid} > S_{solid}$

$\Rightarrow$ the slope is more negative for gas.

Thus, on increasing temperature, the Gibb's function of pure substances decreases, but this decrement is maximum for gaseous phase. Thus, gas phase acquire stability on increasing temperature.



Variation of Gibb's function of pure substances with temperature at constant pressure.

Application of Gibb's Energy (as Measure of Non-Pv Work)

For a pure substance

$dG = d(H - TS) = dH - TdS - SdT$

also $dH = dU + PdV + VdP$

also $dU = dq - PdV - w_{non\text{-}pv}$

($w_{non\text{-}PV}$ = non-PV work done by system)

RELATION BETWEEN FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT

For a general reaction, $mA + nB \rightleftharpoons pC + qD$,

ΔG is given by-

$\Delta G = \Delta G^\circ + 2.303\ RT \log_{10}Q$

where ΔG = Gibb's Free energy change

ΔG° = Standard Gibb's Free energy change, Q = reaction quotient

At equilibrium, $Q = K$, $\Delta G = 0$

$\Rightarrow \Delta G^\circ = -2.303\ RT \log_{10}K$

Train Your Brain

Example 31: 3 moles of $N_2(g)$ originally at 1 atm pressure are mixed isothermally with 5 moles of $H_2(g)$ also at 1 atm pressure to yield a mixture whose total pressure is 1 atm. Assuming ideal behaviour, calculate entropy of mixing.

Sol. Total pressure of mixture = 1 atm

Final pressure of $N_2 = \frac{3}{5+3}(1) = 0.375$ atm

Final pressure of $H_2 = 1 - 0.375 = 0.625$ atm

For N_2, entropy change

$$\Delta S_{N_2} = -nR\ ln\frac{P_2}{P_1} = -2.303 \times 3 \times 8.314 \times \log\left(\frac{0.325}{1}\right)$$

$= 28.03$ J/K

For H_2, entropy change

$$\Delta S_{H_2} = -nR\ ln\frac{P_2}{P_1} = -5 \times 8.314 \times 2.303 \log\frac{0.675}{1}$$

$= 16.34$ J/K.

Total entropy change due to mixing $= \Delta S_{N_2} + \Delta S_{H_2}$

$= 44.37$ J/K.

Example 32: Calculate free energy change for the esterification reaction,

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$.

The equilibrium constant for the reaction at 25°C is 4.

Sol. $\Delta G^\circ = -2.303\ RT \log K = -2.303 \times 8.314 \times 298 \log 4$

$= -(2.303 \times 8.314 \times 298 \times 0.6020) = -3434.92$ J/mol

Credit:--- Divansh.....

Example 33: Calculate ΔG_m for the following process:

(*i*) H_2O (*l*, 100°C 1 atm) $\longrightarrow$ H_2O (g, 100°C, 1 atm)

(*ii*) H_2O (*l*, 100°C, 1 atm) $\longrightarrow$ H_2O (g, 100°C, 0.5 atm)

Sol. (*i*) $\Delta G = 0$ (Equilibrium condition)

(*ii*) H_2O (*l*, 100°C, 1 atm) $\xrightarrow{1}$ H_2O(g, 100°C, 1 atm) $\xrightarrow{2}$ H_2O (g, 100°C, 0.5 atm)

$$\Delta G_1 = 0$$

$$\Delta G_2 = nRT.ln\frac{P_2}{P_1} = 1\times R\times 373\times ln\frac{0.5}{1} = -2149\,J$$

$$\therefore\ \Delta G = \Delta G_1 + \Delta G_2 = -2149\ J$$

Example 34: The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_C is:

Sol. $-\Delta G^\circ = RT\,lnK_C$

Example 35: The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is 75J mol^{-1}. The boiling point of the liquid at 1 atm is:

(*a*) 250 K
(*b*) 400 K
(*c*) 450 K
(*d*) 600 K

Sol. $T = \dfrac{\Delta H_{vap}}{\Delta S_{vap}} = \dfrac{30\times 10^3}{75} = 400K$

Example 36: The positive value of ΔS indicates that-

Sol. The system becomes more disordered

Example 37: For a perfectly crystalline solid, $(C_p)_m = aT^3$, where a is a constant. If $(C_p)_m$ at 10K is 0.375 J/K-mol, then find the value of molar entropy at 20K (in J/K-mol).

Sol. $(C_p)_m = aT^3\ \therefore\ 0.375 = a\,(10)^3\ \therefore\ a = \dfrac{3}{8}\times 10^{-3}$

$$S_m = \int_0^{20}\frac{(C_p)_m dT}{T} = \int_0^{20} aT^2 dT = \left[\frac{aT^3}{3}\right]_0^{20}$$

$$= \frac{8000a}{3} = \frac{8000}{3}\times\frac{3}{8}\times 10^{-3} = 1J/K-mol$$

Concept Application

36. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
(*a*) Endothermic and decreasing disorder
(*b*) Exothermic and increasing disorder
(*c*) Endothermic and increasing disorder
(*d*) Exothermic and decreasing disorder

37. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, then reaction would be spontaneous when:
(*a*) $T = T_e$
(*b*) $T_e > T$
(*c*) $T > T_e$
(*d*) T_e is 5 times T

38. For a reaction at 25°C, enthalpy change (ΔH) and entropy change (ΔS) are -11.7×10^3 J mol and -105 J mol^{-1} K^{-1} respectively. The reaction is:
(*a*) Spontaneous
(*b*) Non spontaneous
(*c*) At equilibrium
(*d*) Can't say anything

39. Identify the correct statement for change of Gibbs energy for a system at constant temperature and pressure.
(*a*) If $\Delta G_{system} > 0$, the process is spontaneous.
(*b*) If $\Delta G_{system} = 0$, the system has attained equilibrium.
(*c*) If $\Delta G_{system} = 0$, the system is still moving in a particular direction.
(*d*) If $\Delta G_{system} < 0$, the process is non spontaneous.

40. In a irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS) satisfy the criteria:
(*a*) $(dS)_{V,E} = 0,\ (dG)_{T,P} = 0$
(*b*) $(dS)_{V,E} = 0,\ (dG)_{T,P} > 0$
(*c*) $(dS)_{V,E} < 0,\ (dG)_{T,P} < 0$
(*d*) $(dS)_{V,E} > 0,\ (dG)_{T,P} < 0$

Aarambh (Solved Examples)

1. The enthalpy change (ΔH) for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is – 92.38 kJ/mol at 298 K. What is value of ΔU at 298K?

Sol. $\Delta U = \Delta H - \Delta n_g RT = -92.38 - (-2) \times \frac{8.314}{1000} \times 298$

$= -87.42$ kJ/mol

2. The heat of combustion of napthalene $\{C_{10}H_8(s)\}$ at constant volume was measured to be – 5133 kJ mol^{-1} at 298K. Calculate the value of enthalpy change (Given R = 8.314 JK^{-1} mol^{-1}).

Sol. The combustion reaction of napthalene.

$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l),$

$\Delta E = -5133$ KJ/mol

$\Delta n_g = 10 - 12 = -2$ mol.

Now applying the relation.

$\Delta H = \Delta E + \Delta n_g RT = -5133 \times 10^3 + (-2)(8.314)(298)$

$= -5133000J - 4955.14\ J = -5137955.14$ joule/mol

3. Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5L, 127°C to 40L. Calculate q, ΔU, w and ΔH, if the process is performed.
   (*i*) Reversibly
   (*ii*) Irreversibly, against a constant external pressure of 0.1 atm.
   (*iii*) As free expansion

Sol. For adiabatic process, q = 0

(*i*) $T.V^{\gamma-1} = \text{constant} \Rightarrow T_1.V_1^{\gamma-1} = T_2.V_2^{\gamma-1}$

$$\therefore\ T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 400 \times \left(\frac{5}{40}\right)^{\frac{5}{3}-1} = 100K$$

Now, $w = \Delta U = nC_v\Delta T = -7482.6J$

$\Delta H = \gamma\Delta U = -12471J$

(*ii*) $\Delta U = w = -P_{ext.}(V_2 - V_1) = 0.1 \times (40-5) \times 101.3 = -354.55J$

and $\Delta H = \frac{5}{3}.\Delta U = -590.92J$

(*iii*) $\Delta U = w = 0$

and $\Delta H = 0$

4. 90 gm water is completely converted into steam at 100°C and 1 atm. Calculate q, ΔU, w and ΔH. Latent heat of vaporisation of water at 100°C is 540 cal/gm.

Sol. $Q = m.L = 90 \times 540 = 48600$ cal

$w = -P(V_{vap} - V_{water}) = -P.V_{vap}$

$= -nRT = -\frac{90}{18} \times 2 \times 373 = -3730$ cal

$\Delta U = q + w = 48600 + (-3430) = 44870$ cal

5. One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decrease by 1 ml. Find ΔU and ΔH.

Sol. $\Delta U = 10J, \Delta H = 990\ J$

$0 + w = \Delta U$

$\Delta U = -P_{ext}(V_2 - V_1)$

$= -100\left(\frac{-1}{1000}\right)$

$= 0.1$ bar litre

$\Delta H = \Delta U + P_2V_2 - P_1V_1$

$\Delta H = 0.1 + \left[\frac{100(99) - (1)(100)}{1000}\right]$

$\Delta H = 0.1 + 9.8$

$\Delta H = 9.9$ bar. litre

$\Delta H = 990$ Joules

6. One mole of an ideal diatomic gas undergoes isobaric expansion from 27°C to 87°C. Calculate q, ΔU, w and ΔH.

Sol. $q = \Delta H = n.C_{p.m}\Delta T = 1 \times \frac{7}{2}R \times 60 = 1745.94J$

$\Delta U = \frac{\Delta H}{\gamma} = 1247.1J$

and $w = -nR.\Delta T = -1 \times 8.314 \times 60 = -498.84J$

7. Five moles of an ideal gas at 300 K is expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q, w, ΔU & ΔH. Calculate the corresponding value of all if the above process is carried out reversibly. (In2 = 0.7)

Sol. $w_{irr} = -1125\ R,\ w_{rev} = -2100R.\ \Delta U = \Delta H = 0,\ q = -w$

8. One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

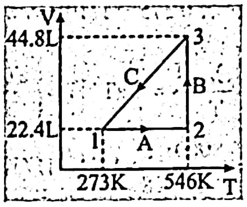


Table-1

State	P	V	T
1			
2			
3			

State	Name of process	q	w	ΔU	ΔH
A					
B					
C					
overall					

Credit:--- Divansh.....

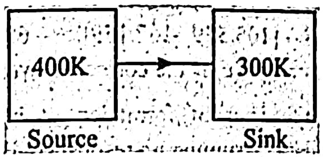
Sol.

Table-1

State	P	V	T
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

State	Name of process	q	w	ΔU	ΔH
A	Isochoric	(3/2) R (273)	0	(3/2) R (273)	(5/2) R(273)
B	Isothermal	546 R ln 2	–546 Rln2	0	0
C	Isobaric	–(5/2) R(273)	–(2/2) R(273)	–(3/2) R (273)	–(5/2) R(273)

9. 100 kJ heat is transferred from a larger heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat:



Find ΔS_{source}, ΔS_{sink} and ΔS_{total} Comment on spontaneity of process.

Sol. (*i*) $\Delta S_{source} = \dfrac{\text{heat absorbed by source}}{\text{Temperature of source}}$

$$\Delta S_{source} = \frac{-100\text{kJ}}{400} = -250\text{J/K}$$

(*ii*) $\Delta S_{sink} = \dfrac{\text{heat absorbed by sink}}{\text{Temperature of sink}}$

$$= \frac{+100000\text{J}}{300} = 333.33\text{J/K}$$

(*iii*) $\Delta S_{total} = \Delta S_{source} + \Delta S_{sink} = +83.33\ \text{J/K}$

10. At what minimum temperature would a given reaction become spontaneous if $\Delta H = +119$ kJ/mol and $\Delta S = +263$ J/K?

(*a*) 452 K (*b*) 2210 K

(*c*) 382 K (*d*) 2.21 K

Sol. $T = \dfrac{\Delta H}{\Delta S} = \dfrac{119\times10^3}{263} = 452.47\text{K}$

Therefore, option (*a*) is the correct answer.

11. Using $G_f^\circ(\text{HI})$ = 1.3 kJ/mole, calculate the standard free energy change for the following reaction,

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

Sol. $\Delta G^\circ = \Sigma G_f^\circ(\text{products}) - \Sigma G_f^\circ(\text{reactants})$

$= 2 \times (1.3) - (0 + 0)$

$= 2.6 - 0 = 2.6$ kJ/mol

12. Calculate the value of K_p at 25°C for an equilibrium reaction, if $\Delta G^\circ = -20$ kJ/mole.

Sol. $\Delta G_p^\circ = -2.303\ RT \log K_p$

$$-20 \times 1000 = -2.303 \times 8.314 \times 298 \log K_p$$

$$\log K_p = \frac{20\times1000}{2.303\times8.314\times298} = 3.505$$

$K_p = \text{antilog}\ (3.505) = 2.91 \times 10^3$

13. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.1 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is 4.2 J g^{-1} K^{-1}, what is the final temperature of water?

Sol. $W = -2.1\ [6 - 4]$

$= -2.1 \times 2$

$= -4.2$ atm × lit. $= -4.2 \times 101.325$ J

This work is used to heat up the water

Specific heat of $H_2O = 4.2\ \dfrac{\text{J}}{\text{gram}\cdot\text{K}}$

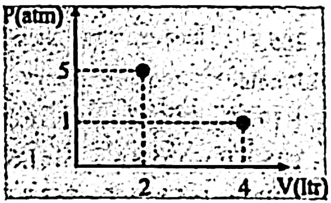
Heat required for increasing temperature by 1°C of 1 mole $= 4.2 \times 18 = 75.6$ J

$4.2 \times 101.325 = 75.6\ [T - 293]$

$5.63 = T - 293$

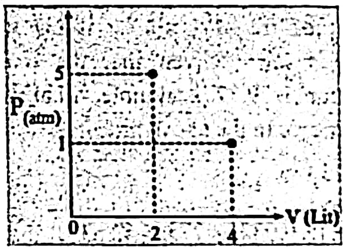
$T = 298.63$ K

14. Following graph shows a single stage expansion process, then workdone by the system is



(*a*) –9104 J (*b*) –202.6 J (*c*) –506 J (*d*) –101.3 J

Sol. $W = -P_{ext}(V_2 - V_1) = -1 \times 2 \times 101.325\ \text{J} = -202.6$ J



Therefore, option (*b*) is the correct answer.

15. One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is:

$[R = 0.082 \text{ L atm mol}^{-1} K^{-1} = 8.3 \text{ J mol}^{-1}K^{-1}]$.

(*a*) 0 (*b*) $R\ln(24.6)$

(*c*) $R\ln(2490)$ (*d*) $3/2\, R\ln(24.6)$

Sol. $\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) = R\ln\left(\frac{P_i}{P_f}\right)$

$$= R\ln\left(\frac{300R}{1\text{ L} \times 1\text{ atm}}\right) = R\ln(24.6)$$

Therefore, option (*b*) is the correct answer.

16. Given the following data:

Substance	ΔH° (kJ/mol)	S°(J/mol K)	ΔG°(kJ/mol)
FeO(s)	−266.3	57.49	−245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	−110.5	197.6	−137.15

Determine at what temperature the following reaction is spontaneous ?

$$FeO(s) + C\,(Graphite) \longrightarrow Fe(s) + CO(g)$$

(*a*) 298 K

(*b*) 668 K

(*c*) 966 K

(*d*) ΔG° is +ve, hence the reaction will never be spontaneous

Sol. $FeO\,(s) + C\,(graphite) \longrightarrow Fe\,(s) + CO\,(g)$

$\Delta H = 0 + [-110.5] - (-266.3)$

$= -110.5 + 266.3$

$= +155.8$ kJ/mole

$\Delta S = 27.28 + 197.6 - 57.49 - 5.74 = 161.65$ J/mole

$\Delta G = \Delta H - T\Delta S = 0 = 155.8 - T \times 161.65 \times 10^{-3}$

$T \times 161.65 \times 10^{-3} = 155.8 \Rightarrow T = 963.8\text{ K}$

Therefore, option (*c*) is the correct answer.

17. What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process?

Sol. $V_1 = 0.025$ L

$$V_2 = \left(\frac{25}{18}\right) \times 0.0821 \times 273 = 42.53\text{ L}$$

$w = -1(42.53 - 0.025) \times 101.325$ J

$= -1025.4$ cal

$$\Delta U = \Delta H - P\Delta v = \left(9.72 \times 1000 \times \frac{25}{18}\right) - 1025.4$$

$= 12474.6$ cal

18. If ΔH_f° for Ag^+ (infinitely diluted), NO_3^- (infinitely diluted), Cl^- (infinitely diluted) and AgCl(s) are 105.579, −207.36, −167.159 and −127.068 kJ/mol respectively. Calculate the enthalpy change for the reaction

$$AgNO_3(aq.) + HCl(aq.) \longrightarrow AgCl(s) + HNO_3\,(aq.)$$

(*a*) 21.471 KJ/mol

(*b*) 145.688 KJ/mol

(*c*) −65.488 KJ/mol

(*d*) None of these

Sol. $\Delta H^\circ_{reaction} = [\Delta H^\circ_f(AgCl) + \Delta H^\circ_f(H^+) + \Delta H^\circ_f(NO_3^-)]$

$- [\Delta H^\circ_f(Ag^+)] + \Delta H^\circ_f(NO_3^-) + \Delta H^\circ_f(Cl^-) + \Delta H^\circ_f(H^+)]$

$= -127.068 - [105.579 - 167.159] = -65.488 \text{ kJ/mol}.$

Therefore, option (*c*) is the correct answer.

19. Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies:

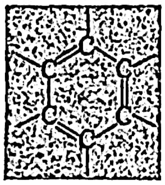
C–C = 83kcal, C = C = 140 kcal, C – H = 99 kcal/mol

Heat of atomisation of C = 170.9 kcal

Heat of atomisation of H = 52.1 kcal

Sol. We have to calculate ΔH for the reaction

$$6C(s) + 3H_2(g) \longrightarrow C_6H_6(g)$$



For reactants:

Heat of atomisation of 6 moles of C = 6 × 170.9 kcal

heat of atomisation of 6 moles of H = 6 × 52.1 kcal

For products:

Heat of formation of 6 moles of C–H bonds = −6 × 99

Heat of formation of 3 moles of C–C = −3 × 83

Heat of formation of 3 moles of C = C bonds = −3 × 140

on adding, we get heat of formation of C_6H_6, i.e.,

$\Delta_f H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140$

$= -75$ kcal/mol

School Level Problems

SINGLE CORRECT TYPE QUESTIONS

1. A gas expands isothermally and reversibly, the work done by a gas is:
(*a*) Zero
(*b*) Maximum
(*c*) Minimum
(*d*) Cannot be determined

2. In a change from state A to state B:
(*a*) "q" depends only on the initial and final state
(*b*) "w" depends only on the initial and final state
(*c*) ΔU depends only on the initial and final state
(*d*) ΔU depends upon the path adopted by "A" to change into "B"

3. The work done when two moles of an ideal gas is compressed from a volume of 5 m^3 to 1 dm^3 at 300 K, under a pressure of 100k Pa is:
(*a*) 499.9 kJ (*b*) –499.9 kJ
(*c*) –99.5 kJ (*d*) 42495 kJ

4. Given:
$NH_3(g) + 3Cl_2(g) \rightleftharpoons NCl_3(g) + 3HCl(g), -\Delta H_1$
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); -\Delta H_2$
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g); \Delta H_3$

The heat of formation of $NCl_3(g)$ in terms of ΔH_1, ΔH_2 and ΔH_3 is:
(*a*) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(*b*) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(*c*) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} + \frac{3}{2}\Delta H_3$
(*d*) None of the above

5. Which reaction, with the following value of ΔH, ΔS at 400 K is spontaneous and endothermic?
(*a*) $\Delta H = -48$ kJ, $\Delta S = +135$ J/K
(*b*) $\Delta H = -48$ kJ, $\Delta S = -135$ J/K
(*c*) $\Delta H = +48$ kJ, $\Delta S = +135$ J/K
(*d*) $\Delta H = +48$ kJ, $\Delta S = -135$ J/K

6. According to third law of thermodynamics, the entropy at 0 K is zero for:
(*a*) Elements in their stable form
(*b*) Perfectly crystalline solids
(*c*) Substance at 1 atm and 25°C
(*d*) N_2O

7. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1} respectively. For the reaction
$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3, \Delta H = -30$ kJ/mole, to be at equilibrium, the temperature should be:
(*a*) 500 K (*b*) 750 K
(*c*) 1000 K (*d*) 1250 K

8. One mole of an ideal gas at 450K is expanded isothermally & reversibly from an initial volume of 5L to 20L. Then, ΔU for the process is–
(*a*) 263.7 cal (*b*) 538.1 cal
(*c*) Zero (*d*) 92.5 cal

ASSERTION AND REASON TYPE QUESTIONS

Directions: These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.
(*a*) Both Assertion and Reason are True and the Reason is a correct explanation of the Assertion.
(*b*) Both Assertion and Reason are True but Reason is not a correct explanation of the Assertion.
(*c*) Assertion is True but the Reason is False.
(*d*) Assertion is False but Reason is True.

9. **Assertion:** The heat absorbed during isothermal expansion of an ideal gas against vacuum is zero.
Reason: The volume occupied by the molecules is zero.

10. **Assertion:** An adiabatic process is a process in which the system does not exchange energy with its surroundings.
Reason: It does not involve any change in temperature of the system.

MATCH THE COLUMN TYPE QUESTIONS

11. Match the following:

	Column-I		Column-II
A.	Adiabatic process	(p)	Heat
B.	Isolated system	(q)	At constant volume
C.	Isothermal change	(r)	No exchange of energy and matter
D.	Path function	(s)	No transfer of heat
E.	$\Delta U = q$	(t)	Constant temperature

(*a*) A-(s); B-(r); C-(t); D-(p); E-(q)
(*b*) A-(p); B-(r); C-(s); D-(t); E-(q)
(*c*) A-(p); B-(q); C-(s); D-(t); E-(r)
(*d*) A-(q); B-(r); C-(s); D-(p); E-(t)

Credit:--- Divansh.....

12. Match the following:

	Column-I		Column-II
A.	Law of Conservation of energy	(p)	First law of thermodynamics
B.	Reversible process	(q)	Infinitely slow process which proceeds through a series of equilibrium states.
C.	Free expansion	(r)	$P_{ext} = 0$
D.	Path function	(s)	At constant pressure

(*a*) A-(s); B-(p); C-(q); D-(r)

(*b*) A-(r); B-(p); C-(s); D-(q)

(*c*) A-(p); B-(q); C-(r); D-(s)

(*d*) A-(s); B-(p); C-(r); D-(q)

HORT ANSWER TYPE QUESTIONS

13. Calculate the work done if 16 g of oxygen gas expands isothermally and reversibly at 300 K from 10 dm³ to 100 dm³.

14. The enthalpy of formation of $CH_4(g)$, $H_2O(g)$ and $CO_2(g)$ are respectively –74.8 kJ mol⁻¹,–285.8 kJ mol⁻¹ and –393.5 kJ/mol. Calculate the standard enthalpy of combustion of $CH_4(g)$.

15. Calculate the entropy change in surroundings when 2.00 mol of $H_2O(l)$ formed under standard conditions.

$\Delta_f H^\ominus = -382$ kJ/mol

16. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol⁻¹. Calculate the internal energy change, when

(i) 1 mol of water is vaporised at 1 bar pressure and 100°C.

(ii) 1 mol of water is converted into ice.

17. The enthalpy change (ΔH) for a reaction is –150 kJ. If the reaction is carried out at constant pressure and releases 200 J of heat, calculate the work done by the system.

18. (i) A chemical reaction releases 240 kJ of heat and does 60 kJ of work on the surroundings. Calculate the change in internal energy (ΔU) for the reaction.

(ii) A chemical reaction takes place at constant pressure and releases 800 J of heat. Calculate the change in enthalpy (ΔH) for the reaction.

LONG ANSWER TYPE QUESTIONS

19. Lattice enthalpy of an ionic compound is defined as the enthalpy change when one mole of an ionic compound dissociates into ions in gaseous state. It is not possible to determine it directly by experiment. Suggest and explain an indirect method to determine lattice enthalpy of NaCl(s).

20. (i) Show that for isothermal expansion of an ideal gas, $\Delta U = 0$ and $\Delta H = 0$.

(ii) Neither q nor w is a state function but q+w is a state function.

(iii) During a process, 802 J of heat is absorbed by the system and 389 J of work is done by the system. Calculate the change in internal energy.

21. (i) Show that for an ideal gas, molar heat capacity at constant volume is equal to 3/2 R.

(ii) Calculate the number of kJ required to raise the temperature of 30 g of aluminium from 40 to 50°C. Given: Molar heat capacity of Al = 24 J mol⁻¹ K⁻¹

22. Explain the concept of spontaneityand Gibbs free energy (ΔG) in detail. Provide examples of reactions with different values of ΔG and explain the implications of these values on the spontaneity of the reactions.

23. One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Calculate q, w, ΔU and ΔH if:

(i) Reversible expansion is carried out

(ii) Irreversible expansion is carried out

CASE STUDY BASED QUESTIONS

24. Imagine you are a scientist working on an experiment involving a gas in a sealed container. You have set up a piston-cylinder system, and you are studying the behavior of the gas as it undergoes various processes. During your experiment, you observe the following:

You start with a gas at a volume of 1.0 L and a pressure of 2.0 atm. The gas is heated, and its volume expands to 2.0 L while maintaining a constant pressure. During this process, you measure the amount of heat added to the system and the work done by the gas.

(i) What does the first law of thermodynamics primarily describe?

(*a*) Conservation of energy

(*b*) Conservation of mass

(*c*) Conservation of momentum

(*d*) Conservation of entropy

(ii) During the process where the gas expands while maintaining a constant pressure, what does the first law of thermodynamics relate to the heat added and the work done by the gas?

(*a*) $\Delta U = q - w$ (*b*) $\Delta U = q + w$

(*c*) $\Delta U = q / w$ (*d*) $\Delta U = q * w$

(iii) If the initial internal energy of the gas is 600 J, and it expands while doing 800 J of work on the surroundings, calculate the final internal energy of the gas.

(*a*) 400 J (*b*) 1400 J

(*c*) 600 J (*d*) 200 J

(iv) If the gas initially had a volume of 2.0 L and it expanded to a final volume of 4.0 L while doing 400 J of work on the surroundings, what is the pressure (in atm) of the gas during this process? (Assume constant temperature.)

(*a*) 0.5 atm (*b*) 1.0 atm

(*c*) 2.0 atm (*d*) 4.0 atm

Prarambh (Topicwise)

THERMODYNAMICS FIRST LAW

Basic Definitions

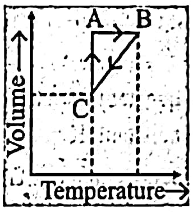
1. Warming ammonium chloride with sodium hydroxide in a test tube is an example of:
   (a) Closed system
   (b) Isolated system
   (c) Open system
   (d) None of these

2. Out of boiling point (I), entropy (II), pH (III) and e.m.f. of a cell (IV), intensive properties are:
   (a) I, II
   (b) I, II, III
   (c) I, III, IV
   (d) All of the above

Thermodynamics Processes & Graph

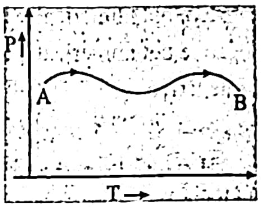
3. An ideal gas filled at pressure of 2 atm and temperature of 300 K, in a balloon is kept in vacuum within a large insulated container. If wall of balloon is punctured, then container's temperature will:
   (a) Decrease
   (b) Increase
   (c) Remain constant
   (d) Unpredictable

4. Five moles of a gas is put through a series of changes as shown graphically in a cyclic process A → B, B → C and C → A respectively corresponding to



   (a) Isochoric, Isobaric, Isothermal
   (b) Isobaric, Isochoric, Isothermal
   (c) Isothermal, Isobaric, Isochoric
   (d) Isochoric, Isothermal, Isobaric

5. The P-T graph as given below was observed for a process on an ideal gas, which of the following statement is true?



   (a) w = +ve, ΔH = +ve
   (b) w = −ve, ΔH = −ve
   (c) w = −ve, ΔH = +ve
   (d) w = +ve, ΔH = −ve

Work Calculation

6. A thermodynamic system goes from state (i) P_1, V to $2P_1, V$ (ii) P, V_1 to $P, 2V_1$ in two different processed. Then work done in the two cases is :
   (a) Zero, Zero
   (b) Zero, $-PV_1$
   (c) $-PV_1$, Zero
   (d) $-PV_1, -P_1V_1$

7. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25°C, is:
   (a) $-2.303 \times 298 \times 0.082 \log 2$
   (b) $-298 \times 10^7 \times 8.31 \times 2.3031 \log 2$
   (c) $-2.303 \times 298 \times 0.082 \log 0.5$
   (d) $-8.31 \times 10^7 \times 298 \times 2.303 \log 0.5$

Heat, Internal Energy, First Law of Thermodynamics, Types of Process

8. In an isochoric process, the increase in internal energy is:
   (a) Equal to the heat absorbed.
   (b) Equal to the heat evolved.
   (c) Equal to the work done.
   (d) Equal to the sum of the heat absorbed and work done.

9. In an isothermal expansion of an ideal gas, select wrong statement:
   (a) There is no change in the temperature of the gas.
   (b) There is no change in the internal energy of the gas.
   (c) The work done by the gas is equal to the heat supplied to the gas.
   (d) The work done by the gas is equal to the change in its internal energy.

10. A system undergoes a process which absorbed 0.5 kJ of heat and undergoes an expansion against external pressure of 1 atm, during the process change in its internal energy is 300 J. Then, predict the change in volume (lit.):
   (a) 1
   (b) 2
   (c) 3
   (d) 4

11. When two moles of hydrogen atoms join together to form a mole of hydrogen molecules in a rigid vessel
   $H(g) + H(g) \longrightarrow H_2(g)$
   then:
   (a) $w < 0$
   (b) ΔU = negative
   (c) q_{system} = positive
   (d) $q_{surrounding}$ = negative

12. If W_1, W_2 & W_3 are magnitude of work done of an ideal gas in an isothermal, adiabatic & isobaric reversible expansion process from same initial state to same final volume (only). Then, correct order will be:

(*a*) $W_3 > W_1 > W_2$ (*b*) $W_3 > W_2 > W_1$
(*c*) $W_2 > W_1 > W_3$ (*d*) $W_1 > W_2 > W_3$

Enthalpy

13. One mole of a non-ideal gas undergoes a change of state (1.0 atm, 3.0 L, 200 K) to (4.0 atm, 5.0 L, 250 K) with a change in internal energy (ΔU) = 40 L-atm. The change in enthalpy of the process in L-atm:

(*a*) 43 (*b*) 57
(*c*) 42 (*d*) None of these

14. A vessel contains 100 litres of a liquid X. Heat is supplied to the liquid in such a fashion that, Heat given = change in enthalpy, the volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, [U - total internal energy]

(*a*) $\Delta U = 0$, $\Delta H = 0$
(*b*) $\Delta U = +202.6\text{J}$, $\Delta H = +202.6\text{ J}$
(*c*) $\Delta U = -202.6\text{J}$, $\Delta H = -202.6\text{ J}$
(*d*) $\Delta U = 0$, $\Delta H = +202.6\text{ J}$

SECOND AND THIRD LAW OF THERMODYNAMICS, ENTROPY

15. Predict which of the following reaction (s) has a positive entropy change?

I. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
II. $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$
III. $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

(*a*) I and II (*b*) III
(*c*) II and III (*d*) II

16. Which of the following reactions is associated with the most negative change in entropy?

(*a*) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
(*b*) $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$
(*c*) $C(s, \text{graphite}) + O_2 \longrightarrow CO_2(g)$
(*d*) $3C_2H_2(g) \longrightarrow C_6H_6(g)$

17. For the gas - phase decomposition,

$PCl_5(g) \overset{\Delta}{\rightleftharpoons} PCl_3(g) + Cl_2(g)$:

(*a*) $\Delta H < 0, \Delta S < 0$ (*b*) $\Delta H > 0, \Delta S > 0$
(*c*) $\Delta H > 0, \Delta S < 0$ (*d*) $\Delta H < 0, \Delta S > 0$

18. Which reaction from the following, will have maximum entropy change?

(*a*) $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$
(*b*) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(*c*) $C(s) + O_2(g) \rightarrow CO_2(g)$
(*d*) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

19. When two mole of an ideal gas $\left(C_{p,m} = \frac{5}{2}R\right)$ is heated from 300 K to 600 K at constant pressure, the change in entropy of gas (ΔS) is:

(*a*) $\frac{3}{2}R\ln 2$ (*b*) $-\frac{3}{2}R\ln 2$
(*c*) $5R\ln 2$ (*d*) $\frac{5}{2}R\ln 2$

20. In previous problem, calculate ΔS_{gas}, if process is carried out at constant volume:

(*a*) $5R\ln 2$ (*b*) $\frac{3}{2}R\ln 2$
(*c*) $3R\ln 2$ (*d*) $-3R\ln 2$

21. Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state and $\Delta H = -401.7\text{ J mol}^{-1}$ for the transition. Assume the surroundings to be an ice-water bath at 0°C:

(*a*) -1.09 J K^{-1} (*b*) 1.47 J K^{-1}
(*c*) 0.38 J K^{-1} (*d*) None of these

Free Energy

22. Which of the following is incorrect regarding Gibb's free energy?

(*a*) It is a state function.
(*b*) It is an extensive property.
(*c*) It is macroscopic property.
(*d*) It is an intensive property.

23. When reaction is in standard state at equilibrium, then:

(*a*) $\Delta H° = 0$
(*b*) $\Delta S° = 0$
(*c*) Equilibrium constant, $K = 0$
(*d*) Equilibrium constant, $K = 1$

24. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?

(*a*) 80 cal (*b*) 540 cal
(*c*) 620 cal (*d*) Zero

25. The enthalpy change for a given reaction at 298 K is $-x$ J mol^{-1} (x being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature:

(*a*) Can be negative but numerically larger than $x/298$.
(*b*) Can be negative but numerically smaller than $x/298$.
(*c*) Cannot be negative.
(*d*) Cannot be positive.

26. A reaction has $\Delta H = -33$ kJ/mol and $\Delta S = -58$ J/K. This reaction would be:

(*a*) Spontaneous at all temperatures.
(*b*) Non-spontaneous at all temperatures.
(*c*) Spontaneous above a certain temperature.
(*d*) Spontaneous below a certain temperature.

27. For a reaction A (g) $\rightleftharpoons$ B(g), at equilibrium, the partial pressure of B is found to be one fourth of the partial pressure of A. The value of ΔG° of the reaction A (g) $\rightleftharpoons$ B(g) is:

(*a*) RT ln 4 (*b*) –RT ln 4
(*c*) RT log 4 (*d*) –RT log 4

28. For a particular reaction $\Delta H^\circ = -76.6$ kJ/mol and $\Delta S^\circ = 226$ J K^{-1}. This reaction is:

(*a*) Spontaneous at all temperatures.
(*b*) Non spontaneous at all temperatures.
(*c*) Spontaneous at temperature below 66°C.
(*d*) Spontaneous at temperature above 66°C.

THERMOCHEMISTRY

Calculation ΔU, ΔH & W

29. The free energy change for a reversible reaction at equilibrium is:

(*a*) Positive (*b*) Negative
(*c*) Zero (*d*) Cannot say

30. Consider the reaction at 300 K

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$; $\Delta H^\circ = -185$ kJ/mol

If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl. What is ΔU° for this reaction?

(*a*) 0 (*b*) –185 kJ/mol
(*c*) 370 kJ/mol (*d*) –370 kJ/mol

31. For which of the following change, $\Delta H \neq \Delta E$?

(*a*) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
(*b*) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$
(*c*) $C(s) + O_2(g) \longrightarrow CO_2(g)$
(*d*) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

32. $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -94.3$ kcal/mol

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -67.4$ kcal/mol

$O_2(g) \longrightarrow 2O(g)$; $\Delta H = 117.4$ kcal/mol

$CO(g) \longrightarrow C(g) + O(g)$; $\Delta H = 230.6$ kcal/mol

Calculate ΔH for $C(s) \longrightarrow C(g)$ in kcal/mol.

(*a*) 171 (*b*) 154
(*c*) 117 (*d*) 145

Enthalpy of Formation & Combustion

33. For the following reaction,

C (diamond) + $O_2 \longrightarrow CO_2(g)$; $\Delta H = -94.3$ kcal/mol

C (graphite) + $O_2 \longrightarrow CO_2(g)$; $\Delta H = -97.6$ kcal/mol

The heat required to change 1 g of C (diamond) $\longrightarrow$ C (graphite) is:

(*a*) 1.59 kcal (*b*) 0.1375 kcal
(*c*) 0.55 kcal (*d*) 0.275 k cal

34. The heat of combustion of sucrose ($C_{12}H_{22}O_{11}$) is 1350 kcal/mol. How much of heat will be liberated when 17.1 g of sucrose is burnt?

(*a*) 67.5 kcal (*b*) 13.5 kcal
(*c*) 40.5 kcal (*d*) 25.5 kcal

35. If $S + O_2 \longrightarrow SO_2$, $\Delta H = -298.2$ kJ $mole^{-1}$

$SO_2 + 1/2\,O_2 \longrightarrow SO_3$, $\Delta H = -98.7$ kJ $mole^{-1}$

$SO_3 + H_2O \longrightarrow H_2SO_4$, $\Delta H = -130.2$ kJ $mole^{-1}$

$H_2 + 1/2\,O_2 \longrightarrow H_2O$, $\Delta H = -287.3$ kJ $mole^{-1}$

then the enthalpy of formation of H_2SO_4 at 298 K will be -

(*a*) –814.4 kJ mol^{-1} (*b*) +814.4 kJ $mole^{-1}$
(*c*) –650.3 kJ $mole^{-1}$ (*d*) –433.7 kJ $mole^{-1}$

36. The values of heat of combustion of ethane (C_2H_6) and ethyne (C_2H_2) are – 341 and – 310 kcal/mol, respectively. Then, which of the following is better fuel on mass basis?

(*a*) C_2H_2 (*b*) C_2H_6
(*c*) Both (*a*) & (*b*) (*d*) None of these

Bond Enthalpy Method & Resonance Energy

37. If enthalpy of dissociation of CH_4 and C_2H_6 are 320 and 600 calories respectively, then bond energy of C–C bond is:

(*a*) 80 cal/mol (*b*) 40 cal/mol
(*c*) 60 cal/mol (*d*) 120 cal/mol

38. The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation for HCl gas will be:

(*a*) –44.0 kcal/mol (*b*) –22.0 kcal/mol
(*c*) 22.0 kcal/mol (*d*) 44.0 kcal/mol

Enthalpy of Solution & Born Haber's Cycle

39. One mole of anhydrous $MgCl_2$ dissolves in water and liberates 25 cal/mol of heat. $\Delta H_{hydration}$ of $MgCl_2 = -30$ cal/mol. Heat of dissolution of $MgCl_2.H_2O$ is:

(*a*) +5 cal/mol (*b*) –5 cal/mol
(*c*) 55 cal/mol (*d*) –55 cal/mol

40. The enthalpy of solution of NaOH (s) in water is – 41.6 kJ/mole when NaOH is dissolved in water then, the temperature of water:

(*a*) Increases (*b*) Decreases
(*c*) Does not change (*d*) Fluctuates

41. The enthalpy change for the reaction of 5 litre of ethylene with 5 litre of H_2 gas at 1.5 atm pressure is $\Delta H = -0.5$ kJ/mol. The value of ΔU will be : (1 atm L = 100 J)

(*a*) – 1.25 kJ/mol (*b*) + 1.25 kJ/mol
(*c*) 0.25 kJ/mol (*d*) – 0.25 kJ/mol

42. Calculate the lattice energy in kJ/mol for the reaction

$Li^+(g) + Cl^-(g) \longrightarrow LiCl(s)$

given that

ΔH_{sub} (Li) = 160 ; ΔH_{diss} (Cl_2) = 244; IP(Li) = 520;

E_A (Cl) = –365 and ΔH_f (LiCl) = – 400 (all in kJ $mole^{-1}$)

(*a*) –837 (*b*) –959 (*c*) –1567 (*d*) –37

Credit:--- Divansh.....

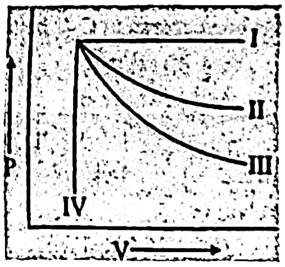
Enthalpy of Neutralization

43. Equal volume of HCOOH and NaOH are mixed. If x is the heat of formation of water, then heat evolved of neutralization is:
(a) More than x
(b) Equal to x
(c) Twice of x
(d) Less than x

44. If heat of dissociation of $CHCl_2COOH$ is 0.7 kcal/mole, then ΔH for the reaction :
$CHCl_2COOH + KOH \longrightarrow CHCl_2COOK + H_2O$
(a) – 13 kcal/mol
(b) + 13 kcal/mol
(c) – 14.4 kcal/mol
(d) – 13.7 kcal/mol

Prabal (JEE Main Level)

1. In which one of the following sets, all the properties belong to same category (all extensive or all intensive)?
(a) Mass, volume, pressure
(b) Temperature, pressure, volume
(c) Heat capacity, density, entropy
(d) Enthalpy, internal energy, volume.

2.


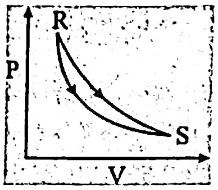
The plots between P and V which represent isochoric and isobaric process respectively:
(a) I, II (b) IV, I (c) I, IV (d) II, III

3. Match the entries of Column-I with appropriate entries of Column-II and choose the correct option out of the four options (A), (B), (C) and (D).

Column-I		Column-II	
A.	Isothermal	(p)	$\Delta T = 0$
B.	Isobaric	(q)	$\Delta V = 0$
C.	Adiabatic	(r)	$\Delta P = 0$
D.	Isochoric	(s)	$q = 0$

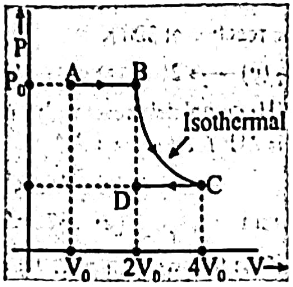
(a) A–p, B–q, C-r, D-s (b) A–p, B–r, C-s, D-q
(c) A–s, B–p, C-r, D-q (d) A–s, B–p, C-q, D-r

4. Consider the cyclic process R → S → R as shown in the Fig. You are told that one of the path is adiabatic and the other one isothermal. Which one of the following is(are) true?



(a) Process R → S is isothermal
(b) Process S → R is adiabatic
(c) Process R → S is adiabatic
(d) Such a graph is not possible

5. Work done for the following process ABCD for given monoatomic ideal gas is:



(a) $w = -2\,P_0\,V_0 \ln 2$ (b) $w = -2\,P_0\,V_0 \ln 2$
(c) $w = -P_0\,V_0\,(1 + \ln 2)$ (d) $w = -P_0\,V_0 \ln 2$

6. 50 L of a certain liquid is confined in a piston system at the external pressure 100 atm. This pressure is suddenly released and liquid is expanded against the constant atmospheric pressure, volume of the liquid increases by 1 L and the final pressure on the liquid is 10 atm. Find the work done.
(a) 1 L.atm (b) 5 L.atm
(c) 500 L.atm (d) 50 L.atm

7. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process in an ideal gas?
(a) Isothermal process : $q = -w$
(b) Cyclic process : $q = -w$
(c) Adiabatic process : $\Delta E = q$
(d) Expansion of a gas into vacuum : $\Delta E = q$

8. One mole of an ideal gas $\left(C_{v,m} = \frac{5}{2}R\right)$ at 300 K and 5 atm is expanded adiabatically to a final pressure of 2 atm against a constant pressure of 2 atm. Final temperature of the gas is:
(a) 270 K (b) 273 K
(c) 248.5 K (d) 200 K

9. The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1 L to 2 L is ΔH_1 and for reversible adiabatic expansion for the same expansion is ΔH_2. Then:

(*a*) $\Delta H_1 > \Delta H_2$

(*b*) $\Delta H_1 < \Delta H_2$

(*c*) $\Delta H_1 = \Delta H_2$, enthalpy being a state function $(\Delta H_1 = \Delta H_2)$

(*d*) $\Delta H_1 = \Delta E_1$ & $\Delta H_2 = \Delta E_2$ where ΔE_1 & ΔE_2 are magnitudes of change in internal energy of gas in these expansions respectively.

10. In which of the following option, the first substance has lesser entropy than the second?

(*a*) (i) Aqueous solution of 1 M of $MgCl_2$.
(ii) Aqueous solution of 1 M of NaCl.

(*b*) (i) Br_2 liquid at 25°C
(ii) Br_2 liquid at 20°C

(*c*) (i) HgO solid
(ii) HgS solid

(*d*) (i) Br_2 liquid
(ii) I_2 solid

11. Select the correct statement(s):

S_1: $AlCl_3$ when dissolved in H_2O, its entropy decreases therefore, it is a non-spontaneous process.

S_2: When H_2 gas is absorbed on the surface of Pd, some amount of heat is released.

S_3: Entropy of D_2 gas is greater than that of H_2 gas.

(*a*) S_1, S_2 & S_3

(*b*) S_1 & S_3

(*c*) S_2 & S_3

(*d*) S_1 & S_2

12. Select the correct statements:

S_1: For every chemical reaction at equilibrium, standard Gibbs free energy change of reaction is zero.

S_2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

S_3: Spontaneity is related to change in entropy of universe.

(*a*) $S_1\ S_2\ S_3$ (*b*) only S_1

(*c*) S_2, S_3 (*d*) S_1, S_3

13. Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all capturing of energy from the reaction is done through electrical process (non P–V work), then calculate maximum available energy which can be captured by combustion of 34.2 g of sucrose.

Given: $\Delta H_{combustion}$ (sucrose) = – 6000 kJ mol^{-1}

$\Delta S_{combustion}$ = 180 J/K mol and body temperature is 300 K

(*a*) 600 kJ (*b*) 594.6 kJ

(*c*) 5.4 kJ (*d*) 605.4 kJ

14. Given the following data:

Substance	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)
FeO(s)	–266.3	57.49	–245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	–110.5	197.6	–137.15

Determine at what temperature the following reaction is spontaneous?

$FeO(s) + C\,(Graphite) \rightarrow Fe(s) + CO(g)$

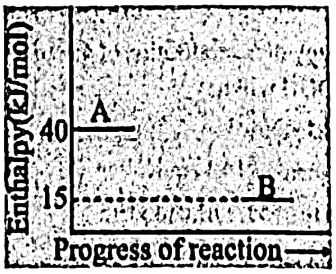
(*a*) 298 K

(*b*) 668 K

(*c*) 964 K

(*d*) ΔG° is +ve, hence the reaction will never be spontaneous

15. Look at the following diagram :



The enthalpy change for the reaction A → B will be:

(*a*) – 25 kJ/mol (*b*) – 40 kJ/mol

(*c*) + 25 kJ/mol (*d*) – 65 kJ/mol

16. In Haber's process of manufacturing of ammonia :

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g);\ \Delta H^0_{25°C} = -92.2$ kJ/mol

Molecule	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$C_P(JK^{-1}\ mol^{-1})$	29.1	28.8	35.1

If C_P is independent of temperature, then reaction at 100°C as compared to that at 25°C will be:

(*a*) More endothermic

(*b*) Less endothermic

(*c*) More exothermic

(*d*) Less exothermic

17. The heat of formation of $C_2H_5OH(\ell)$ is – 66 kcal/mole. The heat of combustion of CH_3OCH_3 (g) is – 348 kcal/mole. ΔH_f for H_2O and CO_2 are –68 kcal/mole and –94 kcal/mole respectively. Then, the ΔH for the isomerisation reaction $C_2H_5OH\ (\ell) \longrightarrow CH_3OCH_3(g)$, and ΔE for the same at T = 25°C are:

(*a*) ΔH = 18 kcal/mole, ΔE = 17.301 kcal/mole

(*b*) ΔH = 22 kcal/mole, ΔE = 21.408 kcal/mole

(*c*) ΔH = 26 kcal/mole, ΔE = 25.709 kcal/mole

(*d*) ΔH = 30 kcal/mole, ΔE = 28.522 kcal/mole

Credit:--- Divansh.....

18. Cesium chloride is formed according to the following equation Cs(s) + 0.5 $Cl_2(g) \rightarrow CsCl(s)$. The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs and electron affinity of chlorine are 81.2, 243.0, 375.7 and 348.3 kJ mol^{-1}. The energy change involved in the formation of CsCl is –388.6 kJ mol^{-1}. Calculate the lattice enthalpy of CsCl.

(*a*) 618.7 kJ mol^{-1}
(*b*) 1237.4 kJ mol^{-1}
(*c*) –1237.4 kJ mol^{-1}
(*d*) –618.7 kJ mol^{-1}

19. The enthalpies of neutralization of a weak base AOH and a strong base BOH by HCl are –12250 cal/ mol and –13000 cal/ mol respectively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was –12500 cal/ mol. In what ratio the acid is distributed between AOH and BOH?

(*a*) 2 : 1
(*b*) 2 : 3
(*c*) 1 : 2
(*d*) None of these

20. The enthalpy of neutralization of 40.0 g of NaOH by 60.0 g of CH_3COOH will be:

(*a*) 57.1 kJ $equiv^{-1}$
(*b*) Less than 57.1 kJ $equiv^{-1}$
(*c*) More than 57.1 kJ $equiv^{-1}$
(*d*) 13.7 kJ $equiv^{-1}$

21. Given $\Delta H^{\circ}_{ionisation}$ (HCN) = 45.2 kJ mol^{-1} and $\Delta H^{\circ}_{ionisation}$ (CH_3COOH) = 2.1 kJ mol^{-1}. Which one of the following facts is true?

(*a*) pK_a (HCN) = pK_a (CH_3COOH)
(*b*) pK_a (HCN) > pK_a (CH_3COOH)
(*c*) pK_a (HCN) < pK_a (CH_3COOH)
(*d*) pK_a (HCN) = (45.17/2.07) pK_a (CH_3COOH)

22. Find the average O–H bond energy in H_2O with the help of following data.

(I) $H_2O(\ell) \longrightarrow H_2O(g)$; $\Delta H = +40.6$ kJ mol^{-1}
(II) $2H(g) \longrightarrow H_2(g)$; $\Delta H = -435.0$ kJ mol^{-1}
(III) $O_2(g) \longrightarrow 2O(g)$; $\Delta H = +489.6$ kJ mol^{-1}
(IV) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$; $\Delta H = -571.6$ kJ mol^{-1}

(*a*) 584.9 kJ mol^{-1}
(*b*) 279.8 kJ mol^{-1}
(*c*) 462.5 kJ mol^{-1}
(*d*) 925 kJ mol^{-1}

23. Enthalpy of polymerisation of ethylene, as represented by the reaction, $nCH_2{=}CH_2 \longrightarrow (-CH_2-CH_2-)_n$ is –100 kJ per mole of ethylene. Given bond enthalpy of C=C bond is 600 kJ mol^{-1}, enthalpy of C–C bond (in kJ/mol) will be:

(*a*) 116.7
(*b*) 350
(*c*) 700
(*d*) Indeterminate

24. The average energy required to break a P–P bond in $P_4(s)$ into gaseous atoms is 53.2 kcal mol^{-1}. The bond dissociation energy of $H_2(g)$ is 104.2 kcal mol^{-1}; ΔH_f^0 of $PH_3(g)$ from $P_4(s)$ is 5.5 kcal mol^{-1}. The P–H bond energy in kcal mol^{-1} is [Neglect presence of Van der Waals forces in $P_4(s)$]

(*a*) 85.2
(*b*) 57.6
(*c*) 78.2
(*d*) 63.3

25. The heat of combustion of yellow phosphorus and red phosphorus are –9.91 kJ/mol and –8.78 kJ/mol respectively. The heat of transition of yellow phosphorus to red phosphorus is

(*a*) –18.69 kJ/mol
(*b*) +1.13 kJ/mol
(*c*) +18.69 kJ/mol
(*d*) –1.13 kJ/mol

26. The bond dissociation energies for Cl_2, I_2 and ICl are 242.3, 151 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mol. What is the standard enthalpy of formation of ICl (g)?

(*a*) –211.3 kJ/mol
(*b*) –14.6 kJ/mol
(*c*) 16.8 kJ/mol
(*d*) 33.5 kJ/mol

27. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1} respectively. For the reaction:

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3 ; \Delta H = -30 \text{ kJ / mol}$$

to be at equilibrium, the temperature should be:

(*a*) 750 K
(*b*) 1000 K
(*c*) 1250 K
(*d*) 500 K

28. ΔH and ΔS for a reaction are +30.558 kJ mol^{-1} and 0.066 kJ K^{-1} mol^{-1} at 1 atm pressure. The temperature at which free energy change is zero and the nature of the reaction below this temperature is

(*a*) 483 K, spontaneous
(*b*) 443 K, non-spontaneous
(*c*) 443 K, spontaneous
(*d*) 463 K, non-spontaneous

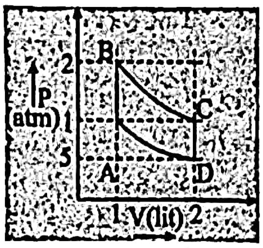
29. The ΔG in the process of melting of ice at 15°C would be

(*a*) ΔG is –ve
(*b*) ΔG is +ve
(*c*) ΔG = 0
(*d*) All of these

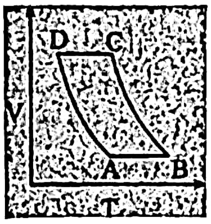
30. How many mL of 1M KOH and 0.5 M H_2SO_4 solutions, respectively when mixed for a total volume of 100 ml produce the highest rise in temperature?

(*a*) 67 : 33
(*b*) 33 : 67
(*c*) 40 : 60
(*d*) 50 : 50

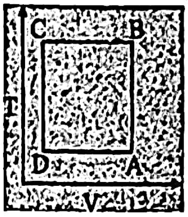
31. A cyclic process ABCD is shown in P-V diagram for an ideal gas, which of the diagram represent the same process?



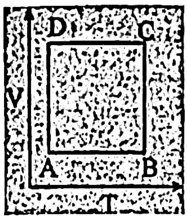
(*a*)



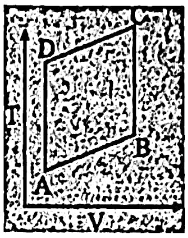
(*b*)



(*c*)



(*d*)



32. 1 mole of NH_3 gas at 27°C is expanded in reversible adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done respectively are:

(*a*) 150 K, –909 cal (*b*) 150 K, –400 cal

(*c*) 250 K, –1000 cal (*d*) 200 K, –800 cal

33. If $\Delta G^0 = -177$ kcal/mol for

(I) $2\,Fe(s) + \frac{3}{2}\,O_2(g) \longrightarrow Fe_2O_3(s)$

and $\Delta G = -19$ kcal/mol

(II) $4\,Fe_2O_3(s) + Fe(s) \longrightarrow 3Fe_3O_4(s)$

What is the Gibbs free energy of formation of $Fe_3O_4(s)$?

(*a*) + 229.6 kcal/mol (*b*) –242.3 kcal/mol

(*c*) –727 kcal/mol (*d*) –229.6 kcal/mol

34. Determine which of the following reactions at constant pressure represent surrounding that do work on the system?

I. $4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g)$

II. $CO(g) + 2H_2(g) \longrightarrow CH_3OH(\ell)$

III. $C(s, graphite) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

IV. $H_2O(s) \longrightarrow H_2O(\ell)$

(*a*) III, IV (*b*) II and III

(*c*) II, IV (*d*) I, II and IV

35. The heat capacity ratio, γ was determined for cyanogen as 1.177. Thus, C_p for this gas is

(*a*) 55.3 $JK^{-1}\,mol^{-1}$

(*b*) 33.26 $JK^{-1}\,mol^{-1}$

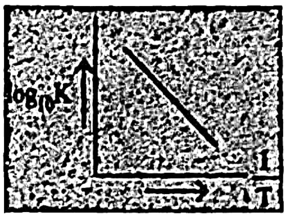
(*c*) 8.314 $JK^{-1}\,mol^{-1}$

(*d*) 24.94 $JK^{-1}\,mol^{-1}$

36. For the dissociation of PCl_5 (g)

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Slope of the linear curve is such that $\theta = \tan^{-1}(-1.5)$



Thus, ΔH° is

(*a*) 28.72 $J\,mol^{-1}$ (*b*) –28.72 $J\,mol^{-1}$

(*c*) 12.47 $J\,mol^{-1}$ (*d*) –12.47 $J\,mol^{-1}$

37. A 50.0 kg person drinks 500 g of milk which has a calorific value of approximately 720 cal g^{-1}. If only 10% of the energy in milk is converted to mechanical work, how high (in meters) can the person climb based on this energy intake?

(*a*) 0.734×10^{-2} m

(*b*) 1.06×10^{2} m

(*c*) 1.22×10^{2} m

(*d*) 3.07×10^{2} m

38. Consider a classroom that is roughly 5m × 10m × 3m. Initially T = 27°C and P = 1 atm. There are 50 people in an insulated class losing energy to the room at the average rate of 150 watt per person. How long can they remain in class if the body temperature is 42°C and person feels uncomfortable above this temperature. Heat capacity of air = (7/2)R

(*a*) 4.34 minutes

(*b*) 5.91 minutes

(*c*) 6.86 minutes

(*d*) 7.79 minutes

39. In order to solve a complex physical chemistry problem, brain requires some "neural energies" which are electrical in nature. Each problem on an average requires 21 Joules of neural energy. Calculate minimum amount of glucose required to solve 10 such problems if all electrical energy is obtained from oxidation of glucose:

[Given: $\Delta H^\circ_{combustion}$ of glucose = – 2800 kJ/mole, $\Delta S^\circ_{combustion}$ of glucose = $-\frac{1000}{3}$ J/mol K, Temperature = 300 K]

(*a*) 14 g (*b*) 14 mg

(*c*) 20 g (*d*) 120 mg

40. At 500 K for an isobaric process,

$\Delta S_{system} = -10\,\frac{kJ}{mol\,K}$ and $\Delta S_{surr} = 12\,\frac{kJ}{mol\,K}$

Therefore, ΔG for the entire process is:

(*a*) – 500 kJ/mol

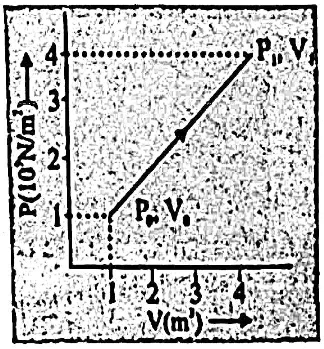
(*b*) – 1000 kJ/mol

(*c*) – 600 kJ/mol

(*d*) – 1100 kJ mol

Credit:--- Divansh.....

41. The work done in changing the state from (P_0, V_0) to (P_1, V_1) in the following system is:



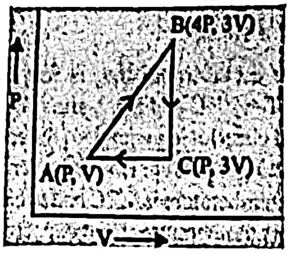
(*a*) -7.5×10^{-5} J

(*b*) -7.5×10^{5} J

(*c*) -7.5×10^{5} erg

(*d*) -7.5×10^{-5} erg

42. The net work done through a series of changes reported in figure at the end of cycle for an ideal gas is equal to:



(*a*) zero (*b*) $-2PV$

(*c*) $-3PV$ (*d*) $-5PV$

43. For an adiabatic expansion of a perfect gas $\Delta P / P$ is equal to:

(*a*) $\frac{\Delta V}{V}$ (*b*) $\gamma\frac{\Delta V}{V}$

(*c*) $-\gamma\frac{\Delta V}{V}$ (*d*) $-\gamma^2\frac{\Delta V}{V}$

44. Given: $\underset{\text{1 mole}}{Fe_2O_3(s)} + 3CO \rightleftharpoons \underset{\text{1 mole}}{2Fe(s)} + 3CO_2; \Delta G_{25^\circ C} = -10 \text{ kJ/mol}$

Find the value of $\Delta G_{25^\circ C}$ for

$$\underset{\text{2 mole}}{2Fe(s) + 3CO_2} \rightleftharpoons \underset{\text{2 mole}}{Fe_2O_3(s) + 3CO}$$

(*a*) + 10 kJ (*b*) + 11.717 kJ

(*c*) 8.28 kJ (*d*) 9.45 kJ

45. In which case of mixing a strong acid and a base each of 1 N concentration, temperature rise is highest?

(*a*) 20 mL acid + 30 mL alkali

(*b*) 10 mL acid + 40 mL alkali

(*c*) 25 mL acid + 25 mL alkali

(*d*) 30 mL acid + 20 mL alkali

INTEGER TYPE QUESTIONS

46. Predict the total number of intensive properties:

(*i*) Free energy (*ii*) Critical density

(*iii*) Viscosity (*iv*) Specific heat capacity

(*v*) molar heat capacity (*vi*) Kinetic energy

(*vii*) Specific gravity (*viii*) Dielectric constant

(*ix*) pH

47. On mixing 0.5 L each of NaOH and HCl rise in temperature has been found as 4°C. On mixing 1 L of each, rise in temperature (in °C) must be_______

48. Two moles of He gas ($\gamma = 5/3$) is initially at temp 27°C and occupy a volume of 20 litres. The gas is first expanded at constant pressure until its volume is doubled, then it undergoes a reversible adiabatic change, until the volume become 110 L, then predict the value of T/100 (where T is the final temperature in kelvin $\left[\left(\frac{4}{11}\right)^{2/3} = \frac{1}{2}\right]$

49. For the reaction at 298 K

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$

If $\Delta H^\circ = -29.8$ Kcal mol^{-1} and $\Delta S^\circ = 0.1$ Kcal K^{-1} mol^{-1} then calculate the value of log K where K is equilibrium constant:

50. Pressure over 1000 mL of a liquid is gradually increased from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate ΔU (in J) of the process, assuming linear variation of volume with pressure.

51. At 500 kilobar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature 'T'. Find the value of $|\Delta H - \Delta U|$ (in kJ/mole) for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T':

52. How many times volume of diatomic gas should be expanded reversibly & adiabatically in order to reduce its r.m.s velocity to half?

Credit:--- Divansh.....

SINGLE CORRECT TYPE QUESTIONS

1. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/°C. Then, the enthalpy change during the process is: (1 L atm = 100 J)

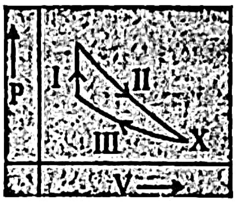
   (*a*) $\Delta H = 15$ kJ/mol (*b*) $\Delta H = 15.7$ kJ/mol

   (*c*) $\Delta H = 14.4$ kJ/mol (*d*) $\Delta H = 14.7$ kJ/mol

2. Assuming the composition of air to be $X(N_2) = 0.80$, $X(O_2) = 0.18$ and $X(CO_2) = 0.02$ molar heat capacity of air at constant pressure is

   (*a*) 3.51 R (*b*) 4.00 R (*c*) 2.50 R (*d*) 3.19 R

3. Initially one mole of ideal gas $\left(C_v = \frac{5}{2}R\right)$ at 1.0 atm and 300 K is put through the following Cycle:



   Step-I: Heating to twice its initial pressure at constant volume.

   Step-II: Adiabatic expansion to its initial temperature.

   Step-III: Isothermal compression back to 1.00 atm.

   What is the volume at state X?

   (*a*) 40.4 L (*b*) 65.0 L (*c*) 139 L (*d*) 4.35 L

4. One mole of a monoatomic ideal gas initially at a pressure of 2.00 bar and a temperature of 273 K is taken to a final pressure of 4.00 bar by a reversible path defined by p/V = constant. Taking C_V to be equal to 12.5 J mol^{-1} K^{-1}, the value of $\Delta U/w$ for this process is calculated to be

   (*a*) −3.0 (*b*) −1.5 (*c*) +1.5 (*d*) +3.0

5. A piston is cleverly designed so that it extracts the maximum amount of work out of a chemical reaction, by matching $P_{external}$ to the $P_{internal}$ at all times. This 8cm diameter piston initially holds back 1 mol of gas occupying 1 L, and comes to rest after being pushed out a further 2 L at 25°C. After exactly half of the work has been done, the piston has travelled out a total of

   (*a*) 10.0 cm (*b*) 11.2 cm (*c*) 14.5 cm (*d*) 20.0 cm

6. Consider the following data : $\Delta_f H°$ (N_2H_4, ℓ) = 50 kJ/mol, $\Delta_f H°$ (NH_3, g) = −46 kJ/mol, B.E. (N-H) = 393 kJ/mol and B.E. (H-H) = 436 kJ/mol,

   $\Delta_{vap}H$ (N_2H_4, ℓ) = 18 kJ/mol

   Calculate the N - N bond energy for N_2H_4.

   (*a*) 190 kJ/mol (*b*) −190 kJ/mol

   (*c*) 95 kJ/mol (*d*) −95 kJ/mol

7. When 1 mole of an ideal gas at 20 atm pressure and 15 L volume expands such that the final pressure becomes 10 atm and the final volume becomes 60 L. Calculate entropy change for the process ($C_{p,m}$ = 30.96 J mole^{-1} K^{-1})

   (*a*) 80.2 J.K^{-1}mol^{-1} (*b*) 62.42 kJ.K^{-1}mol^{-1}

   (*c*) 120 × 10^2 JK^{-1}mol^{-1} (*d*) 27.22 J.K^{-1}mol^{-1}

8. At 1000 K water vapour at 1 atm has been found to be dissociated into H_2 and O_2 to the extent of 3 × 10^{-5}%. The free energy decrease of the system is given by (assuming ideal behaviour.)

   (*a*) $-\Delta G = 90{,}060$ cal (*b*) $-\Delta G = 20$ cal

   (*c*) $-\Delta G = 480$ cal (*d*) $-\Delta G = -45760$ cal

9. Consider the following statements and arrange in the order of true/false as given in the codes.

   S_1: Change in state function between two states is a definite quantity and does not depend on path.

   S_2: Intensive properties can't be algebraically added or subtracted.

   S_3: Ratio of two extensive properties result into a parameter that depends on amount of substance.

   S_4: Molar heat capacity is a path function.

   The correct order of true / false of the above statements is

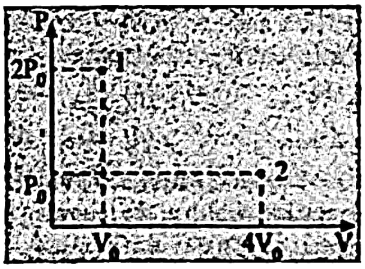
   (*a*) F T F T (*b*) F F F T (*c*) T T F T (*d*) T T T F

10. The enthalpy of neutralization of HNO_3 by NaOH = −13680 cal/eqv. When one equivalent of NaOH is added to a dilute solution containing one equivalent of HNO_3 and one equivalent of a certain monoprotic weak acid 13960 cals are evolved. Assume that the base is distributed between HNO_3 and the weak acid in the ratio 3 : 1 and the weak acid is practically nonionized. Calculate the enthalpy of ionization of the weak acid.

    (*a*) 1120 cal/mol (*b*) 2110 cal/mol

    (*c*) 1320 cal/mol (*d*) 1210 cal/mol

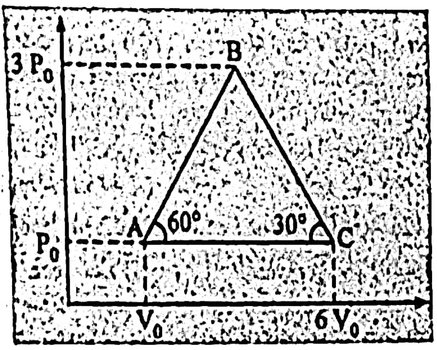
11. A liquid which is confined inside an adiabatic piston is suddenly taken from state-1 to state-2 by a single stage irreversible process. If the piston comes to rest at point 2 as shown, then the enthalpy change for the process will be:



    (*a*) $\Delta H = \dfrac{2\gamma P_0 V_0}{\gamma - 1}$ (*b*) $\Delta H = \dfrac{3\gamma P_0 V_0}{\gamma - 1}$

    (*c*) $\Delta H = -P_0V_0$ (*d*) None of these

12. Two moles of an ideal monoatomic gas undergoes a cyclic process ABCA as shown in the figure. What is the ratio of temperature (in kelvin) of B and A?



(*a*) 1 : 1 (*b*) 3 : 2 (*c*) 27 : 4 (*d*) 9 : 2

13. The work involved (w) in an isothermal expansion of n moles of an ideal gas from an initial pressure of 'P' atm to final pressure of 1 atm in number of steps such that in every step, the constant external pressure exactly 1 atm less than the initial pressure of gas is maintained, is given as

(*a*) $-nRT\sum_{i=1}^{i=P-1}\left(\frac{1}{P+1-i}\right)$ (*b*) $-nRT\sum_{i=1}^{i=P}\left(\frac{1}{P+1-i}\right)$

(*c*) $-nRT\sum_{i=1}^{i=P}\left(\frac{i}{P+1-i}\right)$ (*d*) $-nRT\sum_{i=1}^{i=P-1}\left(\frac{i}{P+1-i}\right)$

MULTIPLE CORRECT TYPE QUESTIONS

14. Which of the following properties of a system are intensive?
(*a*) Color
(*b*) Kinetic energy per mole
(*c*) X (where X = U + H)
(*d*) Specific volume (volume per unit mass)

15. Choose the correct statement(s):
(*a*) System and surrounding are always separated by a real or imaginary boundary.
(*b*) Perfectly isolated system can never be created.
(*c*) In reversible process, energy change in each step can be reversed.
(*d*) Irreversible process is also called quasi-equilibrium state.

16. In an isothermal expansion of a gaseous sample, the correct relation is: (consider w (work) with sign according to new IUPAC convention)

[The reversible and irreversible processes are carried out between same initial and final states.]

(*a*) $w_{rev} > w_{irrev}$ (*b*) $w_{irrev} > w_{rev}$
(*c*) $q_{rev} < q_{irrev}$ (*d*) $\Delta E_{rev} = \Delta E_{irrev}$

17. An ideal gas undergoes adiabatic expansion against constant external pressure. Which of the following is incorrect?
(*a*) Temperature of the system decreases.
(*b*) The relation PV^{γ} = constant will be valid (where P and V are gas variables).
(*c*) $\Delta E + P_{ext}\Delta V = 0$
(*d*) Enthalpy of the gas remains unchanged.

18. In which of the following, entropy increases?
(*a*) Rusting of iron
(*b*) Melting of ice
(*c*) Crystallisation of sugar from solution
(*d*) Vaporisation of camphor

19. The normal boiling point of a liquid 'X' is 400 K. Which of the following statement is true about the process $X(l) \longrightarrow X(g)$?
(*a*) At 400 K and 1 atm pressure $\Delta G = 0$.
(*b*) At 400 K and 2 atm pressure $\Delta G = +$ ve.
(*c*) At 400 K and 0.1 atm pressure $\Delta G = -$ ve.
(*d*) At 410 K and 1 atm pressure $\Delta G = +$ ve.

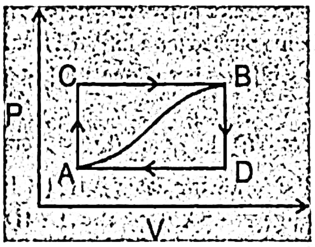
20. Which of the following reaction cannot be used to define the heat of formation of $CO_2(g)$?
(*a*) $CO(g) + \frac{1}{2}O_2 \longrightarrow CO_2(g)$
(*b*) $C_6H_6(\ell) + \frac{7}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell)$
(*c*) $C\,(\text{diamond}) + 2O_2(g) \longrightarrow CO_2(g)$
(*d*) $C\,(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$

21. Find heat of formation of CH_4:
$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -394$ kJ/mol
$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$; $\Delta H = -574$ kJ/mol
$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$; $\Delta H = -892$ kJ/mol
(*a*) –76 kJ/mol (*b*) –18.1 kcal/mol
(*c*) – 244 kJ/mol (*d*) – 50 kcal/mol

22. If $\Delta H^{\circ}_{f(C_2H_6)}(g) = -85$ kJ mol^{-1}, $\Delta H^{\circ}_{f(C_3H_8)}(g) = -104$ kJ mol^{-1}, ΔH° for $C(s) \rightarrow C(g)$ is 718 kJ mol^{-1} and heat of formation of H-atom is 218 kJ mol^{-1}, then:
(*a*) $\Delta H_{C-C} = 345$ kJ (*b*) $\Delta H_{C-H} = 414$ kJ
(*c*) $\Delta H_{H-H} = 436$ kJ (*d*) $\Delta H_{H-H} = 218$ kJ

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 23 to 25): When a system is taken from state A to state B along path ACB as shown in figure below, 80 J of heat flows into the system and the system does 30 J of work.



23. How much heat flows into the system along path ADB if the work done by the system is 10 J?
(*a*) 40 J (*b*) 60 J
(*c*) 80 J (*d*) 100 J

24. When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat and by how much?

(*a*) –70 J ; heat is liberated

(*b*) –60 J ; heat is liberated

(*c*) +70 J ; heat is absorbed

(*d*) +60 J ; heat is absorbed.

25. If $E_D - E_A = -40$ J, the heat absorbed in the processes AD and DB are respectively:

(*a*) $q_{AD} = 30$ J and $q_{DB} = -90$ J

(*b*) $q_{AD} = -60$ J and $q_{DB} = 30$ J

(*c*) $q_{AD} = 30$ J and $q_{DB} = 90$ J

(*d*) $q_{AD} = -30$ J and $q_{DB} = 90$ J

Comprehension (Q. 26 to 28): Entropy is a state function and its value depends on two or three variables temperature (T), pressure (P) and volume (V). Entropy change for an ideal gas having number of moles (n) can be determined by the following equation.

$$\Delta S = 2.303\ nC_V \log\left(\frac{T_2}{T_1}\right) + 2.303\ nR \log\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = 2.303\ nC_p \log\left(\frac{T_2}{T_1}\right) + 2.303\ nR \log\left(\frac{P_1}{P_2}\right)$$

Since free energy change for a process or a chemical equation is a deciding factor for spontaneity, which can be obtained by using entropy change (ΔS) according to the expression, $\Delta G = \Delta H - T\Delta S$ at a temperature T.

26. What would be the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 L to a volume of 50 L at 25°C? [Given R = 8.3 J/mole K]

(*a*) 38.23 J/K (*b*) 26.76 J/K

(*c*) 20J/K (*d*) 28.23J/K

27. An isobaric process having one mole of an ideal gas has entropy change 23.03 J/K for the temperature range 27°C to 327°C. What would be the molar specific heat capacity (C_V) ?

(*a*) $\frac{10}{\log 2}$ J/K mol (*b*) $\frac{10}{\log 2} - 8.3$ J/K mol

(*c*) 10 × log2 J/K mol (*d*) 10 log2 + 8.3 J/K mol

28. For a reaction $M_2O(s) \longrightarrow 2M(s) + \frac{1}{2}O_2(g)$; $\Delta H = 30$ kJ/mol and $\Delta S = 0.07$ kJ/K-mol at 1 atm. Calculate upto which temperature the reaction would not be spontaneous?

(*a*) $T > 428.6$ K (*b*) $T > 300.8$ K

(*c*) $T < 300.8$ K (*d*) $T < 428.6$ K

Comprehension (Q. 29 to 31): An ideal gas whose adiabatic exponent equals γ is expanded according to the law $P = \alpha V$, where α is a constant. The initial volume of the gas is equal to V_0. As a result of expansion, the volume increases 4 times.

29. What is the increment of the internal energy of the gas?

(*a*) $\frac{15\alpha V_0^2}{\gamma - 1}$ (*b*) $\frac{\alpha V_0^2}{\gamma - 1}$

(*c*) $\frac{15\alpha V_0^2}{2}$ (*d*) $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$

30. What is the magnitude of work performed by the gas?

(*a*) $\frac{15\alpha V_0^2}{\gamma - 1}$ (*b*) $\frac{\alpha V_0^2}{\gamma - 1}$

(*c*) $\frac{15\alpha V_0^2}{2}$ (*d*) $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$

31. What is the molar heat capacity of the gas in the process?

(*a*) $\frac{R(\gamma+1)}{2(\gamma-1)}$ (*b*) $\frac{\alpha V_0^2}{\gamma - 1}$

(*c*) $\frac{R(\gamma-1)}{2(\gamma+1)}$ (*d*) $\frac{15\alpha(\gamma+1)V_0^2}{2(\gamma-1)}$

Comprehension (Q. 32 to 34): A horizontal piston-cylinder arrangement is placed in a constant temperature bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial gas pressure of 14 bar. The initial gas volume is 0.03 m^3. The external force on the piston is reduced gradually, allowing the gas to expand until its volume doubles.

32. Calculate the value of 1000 |W| where W is work done (in bar. m^3) by the gas in moving the external force.

(*a*) 167 (*b*) 294 (*c*) 358 (*d*) 192

33. Calculate the value of 100 |W| where W is work done (in bar. m^3) by the gas if the same expansion is carried out by removing a part of the external force suddenly.

(*a*) 11 (*b*) 33 (*c*) 21 (*d*) 44

34. Calculate % efficiency of this process as compared with the reversible process (% of reversible work).

Report your answer as (% efficiency × 0.7).

(take $\ell n2 = 0.7$)

(*a*) 70 (*b*) 80 (*c*) 30 (*d*) 50

Comprehension (Q. 35 to 36): 1 mole of an ideal gas, initially at 400 K and 10 atm is first expanded at constant pressure till the volume is doubled. Then the gas is made to undergo an isochoric process, in which its temperature is found to decrease to 'V' K. In the last final step, gas was compressed reversibly and adiabatically to initial state.

35. Find the value of V.

(*a*) 143 (*b*) 364 (*c*) 252 (*d*) 293

36. Determine the net work involved in this cyclic process (in terms of R) as W. If |W| = 2 R × z, find the value of z.

Given, C_V for gas = 1.5 R, $(4)^{-1/3} = 0.63$.

(*a*) 29 (*b*) 49 (*c*) 69 (*d*) 89

Comprehension (Q. 37 to 38): Reaction of gaseous fluorine (F_2) with compound X yields a single product Y, whose mass percent composition is 61.7% F and 38.3% Cl.

$$2ClF\,(g) + O_2\,(g) \rightarrow Cl_2O\,(g) + OF_2\,(g) \qquad \Delta H° = 205.6\ kJ/mol$$

$$2ClF_3\,(g) + 2O_2\,(g) \rightarrow Cl_2O\,(g) + 3OF_2\,(g) \qquad \Delta H° = 533.0\ kJ/mol$$

$$\Delta_f H°\,(OF_2, g) = 24.7\ kJ/mol$$

37. Find the correct match
(*a*) $X : ClF, Y : ClF_3$ (*b*) $X : ClF_3, Y : ClF$
(*c*) $X : ClF, Y : ClF_5$ (*d*) $X : ClF_5, Y : ClF$

38. Calculate the magnitude of $\Delta_f H°$ (in kJ/mol) for the synthesis of Y.
(*a*) 139 (*b*) 119 (*c*) 179 (*d*) 209

MATCH THE COLUMN TYPE QUESTIONS

39. Match Column-I with Column-II.

	Column-I		Column-II
A.	Reversible isothermal expansion of an ideal gas.	p.	$w = -2.303\ nRT \log\left(\frac{V_2}{V_1}\right)$
B.	Reversible adiabatic compression of an ideal gas.	q.	$PV^\gamma = \text{constant}$
C.	Irreversible adiabatic expansion of an ideal gas.	r.	$w = \frac{nR}{(\gamma - 1)}(T_2 - T_1)$
D.	Irreversible isothermal compression of an ideal gas.	s.	$\Delta H = 0$

(*a*) A-(p, s); B-(q, r); C-(r); D-(s)
(*b*) A-(p); B-(r); C-(p, r); D-(s,q)
(*c*) A-(p, q); B-(p, s); C-(r); D-(s)
(*d*) A-(s); B-(p, r); C-(p, r); D-(q, p)

40. Match Column-I with Column-II

	Column-I		Column-II
A.	$(\Delta G_{system})_{T,P} = 0.$	p.	Process is in equilibrium
B.	$\Delta S_{system} + \Delta S_{surrounding} > 0$	q.	Process is non-spontaneous
C.	$\Delta S_{system} + \Delta S_{surrounding} < 0$	r.	Process is spontaneous
D.	$(\Delta G_{system})_{T,P} > 0$	s.	System is unable to do useful work

(*a*) A-(q, s); B-(r); C-(p, s); D-(q, s)
(*b*) A-(q,s); B-(r); C-(q, s); D-(p, s)
(*c*) A-(p,s); B-(r); C-(q, s); D-(q, s)
(*d*) A-(p,s); B-(s); C-(r); D-(q, s)

41. Match Column-I with Column-II.

	Column-I		Column-II
A.	$C\,(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$	p.	$\Delta H°_{combustion}$
B.	$C(s, \text{graphite}) \longrightarrow C(g)$	q.	$\Delta H°_{formation}$
C.	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	r.	$\Delta H°_{atomization}$
D.	$CH_4(g) \longrightarrow C(g) + 4H(g)$	s.	$\Delta H°_{sublimation}$

(*a*) A-(q,r,s); B-(p,r,s); C-(p,q); D-(r)
(*b*) A-(r,s); B-(q,r,s); C-(p); D-(p,s)
(*c*) A-(p); B-(q,s); C-(p,q,r); D-(r)
(*d*) A-(p,q); B-(q,r,s); C-(p); D-(r)

42. List-I and List-II contains four entries each. Entries of List-I are to be matched with some entries of List-II. One or more than one entries of List-I may have the matching with the same entries of List-II and select the correct answer using the code given below the lists:

	List-I		List-II
A.	Reversible cooling of an ideal gas at constant volume	p.	$w = 0; q < 0; \Delta U < 0$
B.	Reversible isothermal expansion of an ideal gas	q.	$w < 0; q > 0; \Delta U > 0$
C.	Adiabatic expansion of non-ideal gas into vacuum	r.	$w = 0; q = 0; \Delta U = 0$
D.	Reversible melting of sulphur at normal melting point	s.	$w < 0; q > 0; \Delta U = 0$

(*a*) A-(p); B-(s); C-(r); D-(q)
(*b*) A-(p); B-(s); C-(s); D-(q)
(*c*) A-(s); B-(p); C-(r); D-(q)
(*d*) A-(p); B-(r); C-(r); D-(q)

INTEGER TYPE QUESTIONS

43. A sample of an ideal gas is expanded from 1 dm^3 to 3 dm^3 in a reversible process for which $P = KV^3$, with $K = 1/5\ (atm/dm^3)$, what is magnitude of work done by gas (in L atm)?

44. The valve on a cylinder containing initially 1 litre of an ideal gas at 7 atm and 25°C is opened to the atmosphere, whose pressure is 760 torr and the temperature is 25°C. Assuming that the process is isothermal, what is magnitude of work (in L atm) done on the atmosphere by the action of expansion?

45. 2 mole of ideal monoatomic gas was subjected to reversible adiabatic compression from initial state of $P = 1$ atm and $T = 300$ K till the pressure is $4\sqrt{2}$ atm and temperature is T K. The gas is then subjected to reversible isothermal expansion at T K till the internal pressure is one atm. The gas is now isobarically cooled to attain initial state. Find $|W_{Net}|$ (in calorie) for whole process.

[Use ln 2 = 0.7, R = 2 cal/K-mol]

46. 1 mole & 2 mole respectively of two ideal gases A ($C_v = 3R$) and B ($C_v = \frac{3}{2}R$) are taken in a container and expanded reversibly and adiabatically from $V = 1$ L to $V = 4$ L starting from initial temperature $T = 320$ K. Find $|\Delta H|$ for the process (in cal).

47. The K_p for reaction $A + B \rightleftharpoons C + D$ is 2.0 at 27°C and 8.0 at 127°C. Determine $\Delta H°$ (in kJ/mol) for the reaction over this range of temperature ($\ln 2 = 0.7$)?

48. Di-oxygen is heated from 300 to 600 K at a constant pressure of 1 bar. What is the value of increase in molar entropy (in $JK^{-1}mol^{-1}$)? The molar heat capacity (in $J\,K^{-1}\,mol^{-1}$) for the O_2 is $C_{p,m} = 10 + 10^{-2}T$

(Given: $\ln 2 = 0.7$)

49. Calculate the magnitude of enthalpy of combustion (in kJ mol^{-1}) of methyl alcohol (*l*) at 298 K from the following data:

Bond	C-H	C–O	O–H	O=O	C=O
Bond Enthalpy (kJ mol^{-1})	414	351.5	464.5	494	711

Resonance energy of $CO_2 = -143$ kJ mol^{-1}

Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol^{-1}.

Latent heat of vaporisation of water = 40.6 kJ mol^{-1}.

50. 1 mol of a liquid of molar volume 100 mL is kept in an adiabatic container under a pressure of 1 bar. The pressure is steeply increased to 100 bar. Under this constant pressure of 100 bar, the volume of the liquid decreases by 1 mL. Calculate ΔU (in J) of the process.

51. A mixture of di-hydrogen gas with the theoretical amount of air at 298 K and a total pressure of 1 atmosphere is exploded in a closed rigid vessel. The mean heat capacities at constant volume for di-nitrogen and Water vapours in the temperature range 298 K to 3000 K are respectively 26.36 $JK^{-1}\,mol^{-1}$ and 38.91 $JK^{-1}mol^{-1}$. If the enthalpy of the reaction.

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g)$$

at constant volume is -240.58 kJ mol^{-1}, calculate the maximum explosion temperature (in kelvin) assuming adiabatic conditions.

NUMERICAL TYPE QUESTIONS

52. To what pressure (in atm) must a certain ideal gas ($\gamma = 1.4$) at 373 K and 1 atmosphere pressure be compressed adiabatically in order to raise its temperature to 673 K?

(Answer upto two decimal place)

53. A system undergoes a certain change in state by path I and the corresponding heat-absorbed and the work term are 10 K. cal and 0 erg. respectively. For the same change in state by path II the respective quantities are 11K. cal and $0.5\,W_{max}$ where W_{max} represents the work if the specified change is reversibly carried out. Find W_{max} (in terms of 10^{10} ergs)

(Answer upto one decimal place)

54. Two equal rectangular blocks are respectively at temperatures of 500 K and 200 K. Each has a weight of 500 g and a specific heat of 0.1 cal. K^{-1} $gram^{-1}$. The blocks are put in contact till both have the same temperature. What would be the entropy change (in Cal/K) for the blocks?

(Answer upto one decimal place)

55. Calculate the entropy change (in kJ/K/mol) when one kilogram water at 27°C is converted to superheated steam at 200°C under constant atmospheric pressure. (Specific heat of liquid water = 4180 J/kg. K, specific heat of steam = 1670 + 0.49 T J/kg. K at T K and latent heat of vaporisation = 23 × 10^5 J/kg)

(Answer upto two decimal place)

PYQ's (Past Year Questions)

THERMODYNAMIC TERMS

1. What happens when methane undergoes combustion in systems A and B respectively? **[13 April, 2023 (Shift-II)]**

Adiabatic system	Diathermic container
System A	System B

(*a*)

System A	System B
Temperature rises	Temperature remains same

(*b*)

System A	System B
Temperature falls	Temperature rises

(*c*)

System A	System B
Temperature falls	Temperature remains same

(*d*)

System A	System B
Temperature remains same	Temperature rises

2. The total number of intensive properties from the following is________.

Volume, Molar heat capacity, Molarity, E^0 cell, Gibbs free energy change, Molar mass, Mole

[11 April, 2023 (Shift-II)]

3. Among the following the number of state variable is ___________. **[28 July, 2022 (Shift-II)]**

Internal energy (U)	Volume (V)
Heat (q)	Enthalpy (H)

4. Among the following the set of parameters that represents path function is: **[9 April, 2019 (Shift-I)]**

(A) $q + w$ (C) q

(B) w (D) $H - TS$

(*a*) (B) and (C) (*b*) (B), (C) and (D)

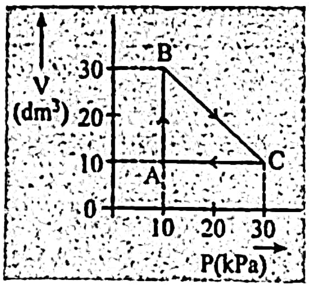
(*c*) (A), (B) and (C) (*d*) (A) and (D)

FIRST LAW OF THERMODYNAMICS AND APPLICATIONS OF WORK DONE

5. If three moles of an ideal gas at 300 K expand isothermally from 30 dm^3 to 45 dm^3 against a constant opposing pressure of 80 kPa, then the amount of heat transferred is_______ J.

[27 Jan, 2024 (Shift-I)]

6.



An ideal gas undergoes a cyclic transformation starting from the point A and coming back to the same point by tracing the path $A \rightarrow B \rightarrow C \rightarrow A$ as shown in the diagram. The total work done in the process is _____ J.

[30 Jan, 2024 (Shift-I)]

7. If 5 moles of an ideal gas expands from 10 L to a volume of 100 L at 300 K under isothermal and reversible condition then work, w, is $-x$ J. The value of x is ______.
(Given $R = 8.314\ J\ K^{-1}\ mol^{-1}$) **[31 Jan, 2024 (Shift-II)]**

8. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following:

[01 Feb, 2024 (Shift-I)]

(*a*) $q = 0, \Delta T \neq 0, w = 0$ (*b*) $q = 0, \Delta T < 0, w \neq 0$

(*c*) $q \neq 0, \Delta T = 0, w = 0$ (*d*) $q = 0, \Delta T = 0, w = 0$

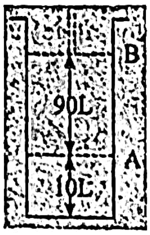
9. Three moles of an ideal gas are compressed isothermally from 60 L to 20 L using constant pressure of 5 atm. Heat exchange Q for the compression is – ____ Lit. atm.

[04 April, 2024 (Shift-II)]

10. An ideal gas, $\bar{C}_V = \frac{5}{2}R$, is expanded adiabatically against a constant pressure of 1 atm until it doubles in volume. If the initial temperature and pressure is 298K and 5 atm, respectively, then the final temperature is_______ K (nearest integer).
[$\bar{C}_V$ is the molar heat capacity at constant volume]

[06 April, 2024 (Shift-I)]

11.



Consider the figure provided.

1 mol of an ideal gas is kept in a cylinder, fitted with a piston, at the position A, at 18°C. If the piston is moved to position B, keeping the temperature unchanged, then 'x' L atm work is done in this reversible process.

x = ______ L atm. (nearest integer)

[Given: Absolute temperature = °C + 273.15, $R = 0.08206\ L\ atm\ mol^{-1}\ K^{-1}$] **[08 April, 2024 (Shift-I)]**

12. 1 mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. The work done is 3 kJ mol^{-1}. The final temperature of the gas is _______ K (Nearest integer). Given $C_v = 20\ J\ mol^{-1}K^{-1}$.

[30 Jan, 2023 (Shift-II)]

13. When 2 litre of ideal gas expands isothermally into vacuum to a total volume of 6 litre, the change in internal energy is _______ J. (Nearest integer)

[30 Jan, 2023 (Shift-I)]

14. When 5 moles of He gas expand isothermally and reversibly at 300 K from 10 litre to 20 litre, the magnitude of the maximum work obtained is_______ J. (nearest integer)
[Given: $R = 8.3\ JK^{-1}\ mol^{-1}$ and $\log 2 = 0.3010$]

[27 June, 2022 (Shift-II)]

Credit:--- Divansh.....

15. 4.0 L of an ideal gas is allowed to expand isothermally into vacuum until the total volume is 20L. The amount of heat absorbed in this expansion is_______ L atm.

[28 June, 2022 (Shift-I)]

16. Five moles of an ideal gas at 293 K is expanded isothermally from an initial pressure of 2.1 MPa to 1.3 MPa against at constant external pressure 4.3 MPa. The heat transferred in this process is_____ kJ mol^{-1}. (Rounded-off to the nearest integer).

[Use R = 8.314 J mol^{-1} K^{-1}] [25 Feb, 2021 (Shift-II)]

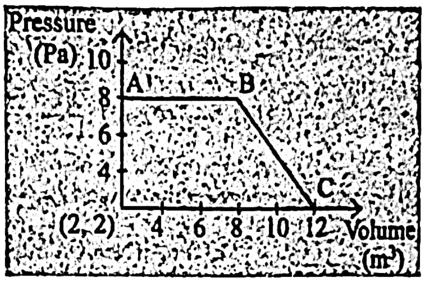
17. At 25°C, 50 g of iron reacts with HCl to form $FeCl_2$. The evolved hydrogen gas expands against a constant pressure of 1 bar. The work done by the gas during this expansion is _________ J. (Round off to the nearest integer).

[Given: R= 8.314 J mol^{-1} K^{-1}. Assume hydrogen is an ideal gas]

[Atomic mass of Fe is 55.85u]

[16 March, 2021 (Shift-II)]

18. The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is _________ [8 Jan, 2020 (Shift-I)]



19. In thermodynamics the P-V work done is given by

$$w = -\int dV P_{ext}.$$

For a system undergoing a particular process, the work done is,

$$w = -\int dV\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)$$ [JEE Adv 2020]

This equation is applicable to a:

(a) System that satisfies the van der Waals equation of state.

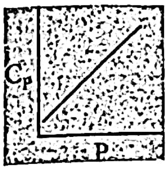
(b) Process that is reversible and isothermal.

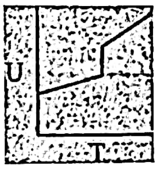
(c) Process that is reversible and adiabatic.

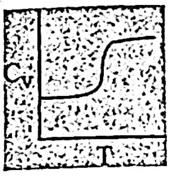
(d) Process that is irreversible and at constant isothermal.

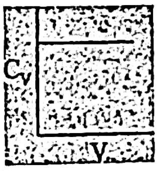
20. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?

[12 Jan, 2019 (Shift-I)]

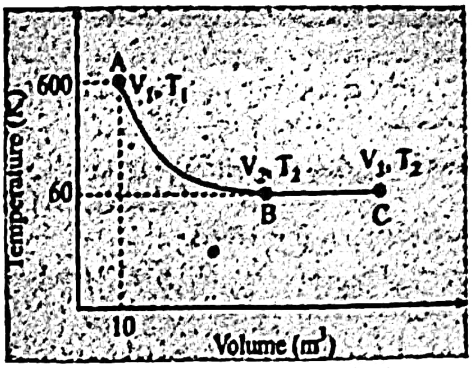
(a)


(b)


(c)


(d)


21. One mole of an ideal monoatomic gas undergoes two reversible processes (A → B and B → C) as shown in the given figure: [JEE Adv 2023]

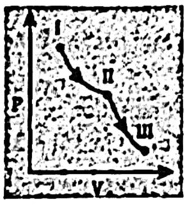


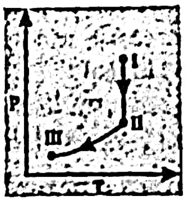
A → B is an adiabatic process. If the total heat absorbed in the entire process (A → B and B → C) is RT_2 ln 10, the value of 2 log V_3 is ________.

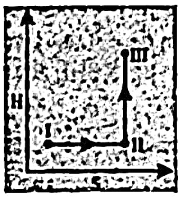
[Use, molar heat capacity of the gas at constant pressure, $C_{p,m}$ = 5/2R]

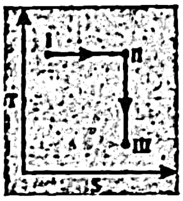
22. An ideal gas undergoes a reversible isothermal expansion from state I to state II followed by a reversible adiabatic expansion from state II to state III. The correct plot(s) representing the changes from state I to state III is (are) (p:pressure, V:volume, T:temperature, H:enthalpy, S:entropy

[JEE Adv 2021]

(a)


(b)


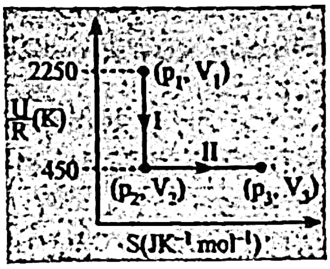
(c)


(d)


23. One mole of an ideal gas at 900 K, undergoes two reversible processes, I followed by II, as shown below. If the work done by the gas in the two process are same, the value of ln $\frac{V_3}{V_2}$ is: [JEE Adv 2021]

(U: internal energy, S: entropy, P: pressure, V: volume, R: gas constant)

(Given: molar heat capacity at constant volume, $C_{v,m}$ of the gas is $\frac{5}{2}$R)



ENTHALPY CHANGE, ΔH OF A REACTION & ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

24. Standard enthalpy of vapourisation for CCl_4 is 30.5 kJ mol^{-1}. Heat required for vapourisation of 284g of CCl_4 at constant temperature is ____kJ.

(Given molar mass in g mol^{-1}; C = 12, Cl = 35.5)
[29 Jan, 2024 (Shift-II)]

25. Two reactions are given below:

$2Fe_{(s)} + 3/2O_{2(g)} \rightarrow Fe_2O_{3(s)}, \Delta H^\circ = -822 kJ/mol$

$C_{(s)} + 1/2O_{2(g)} \rightarrow CO_{(g)}, \Delta H^\circ = -110 kJ/mol$

Then enthalpy change for following reaction

$3C_{(s)} + Fe_2O_{3(s)} \rightarrow 2Fe_{(s)} + 3CO_{(g)}$ is ______ kJ/mol
[30 Jan, 2024 (Shift-II)]

26. The enthalpy of formation of ethane (C_2H_6) from ethylene by addition of hydrogen where the bond energies of C – H, C – C, C = C, H – H are 414 kJ, 347 kJ, 615 kJ and 435 kJ respectively is - __________ kJ.
[04 April, 2024 (Shift-I)]

27. Given below are two statements: One is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**

Assertion (A): Enthalpy of neutralisation of strong monobasic acid with strong monoacidic base is always −57 kJ mol^{-1}

Reason (R): Enthalpy of neutralisation is the amount of heat liberated when one mole of H^+ ions furnished by acid combine with one mole of ^-OH ions furnished by base to form one mole of water. In the light of the above statements, choose the correct answer from the options given below.
[05 April, 2024 (Shift-I)]

(*a*) (A) is true but (R) is false

(*b*) Both (A) and (R) are true and (R) is the correct explanation of (A)

(*c*) (A) is false but (R) is true

(*d*) Both (A) and (R) are true but (R) is not the correct explanation of (A)

28. The heat of combustion of solid benzoic acid at constant volume is −321.30 kJ at 27°C. The heat of combustion at constant pressure is (−321.30 – *xR*) kJ, the value of *x* is __________.
[05 April, 2024 (Shift-I)]

29. Combustion of 1 mole of benzene is expressed at

$$C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow CO_2(g) + 3H_2O(l)$$

The standard enthalpy of combustion of 2 mol of benzene is – '*x*' kJ.

x = ______.
[05 April, 2024 (Shift-II)]

(1) Standard Enthalpy of formation of 1 mol of $C_6H_6(l)$, for the reaction

$6C(graphite) + 3H_2(g) \rightarrow C_6H_6(l)$ is 48.5 kJ mol^{-1}.

(2) Standard Enthalpy of formation of 1 mol of $CO_2(g)$, for the reaction

$C(graphite) + O_{2(g)} \rightarrow CO_2(g)$ is −393.5 kJ mol^{-1}.

(3) Standard and Enthalpy of formation of $H_2O(l)$, for the reaction

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ is −286 kJ mol^{-1}.

30. $\Delta_{vap}H^\circ$ for water is +40.49 kJ mol^{-1} at 1 bar and 100°C. Change in internal energy for this vapourisation under same condition is ______ kJ mol^{-1}. (Integer answer)
(Given R = 8.3 JK^{-1} mol^{-1})
[08 April, 2024 (Shift-II)]

31. The heat of solution of anhydrous $CuSO_4$ and $CuSO_4 \cdot 5H_2O$ are −70 kJ mol^{-1} and +12 kJ mol^{-1} respectively.
The heat of hydration of $CuSO_4$ to $CuSO_4 \cdot 5H_2O$ is −x kJ.
The value of x is_____.
[09 April, 2024 (Shift-I)]

32. Given
[10 April, 2023 (Shift-I)]

(A) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\quad \Delta H_1^0 = -x$ kJ mol^{-1}

(B) $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H_2^0 = -y$ kJ mol^{-1}

The ΔH^0 for the reaction

$C(graphite) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ is

(*a*) $\frac{x-2y}{2}$ (*b*) $\frac{x+2y}{2}$ (*c*) $\frac{2x-y}{2}$ (*d*) $2y - x$

33. The enthalpy change for the conversion $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq.)$ is (–) __________ kJ mol^{-1}(Nearest integer)

Given, $\Delta_{dis}H^o_{Cl_{2(g)}} = 240 kJmol^{-1}$

$\Delta_{eg}H^o_{Cl_{(g)}} = -350 kJmol^{-1}$

$\Delta_{hyd}H^o_{Cl^-_{(g)}} = -380 kJmol^{-1}$
[31 Jan, 2023 (Shift-I)]

34. When a 60W electric heater is immersed in a gas for 100s in a constant volume container with adiabatic walls, the temperature of the gas rises by 5°C. The heat capacity of the given gas is ______J K^{-1} (Nearest integer)
[8 April, 2023 (Shift-I)]

35. At 25°C and 1 atm pressure, the enthalpy of combustion of benzene (l) and acetylene (g) are −3268 kJ mol^{-1} and −1300 kJ mol^{-1}, respectively. The change in enthalpy for the reaction $3C_2H_2(g) \rightarrow C_6H_6(l)$, is
[25 June, 2022 (Shift-II)]

(*a*) +324 kJ mol^{-1} (*b*) +632 kJ mol^{-1}

(*c*) −632 kJ mol^{-1} (*d*) −732 kJ mol^{-1}

36. At 25°C and 1 atm pressure, the enthalpies of combustion are as given below:
[24 June, 2022 (Shift-II)]

Substance	H_2	C (graphite)	$C_2H_6(g)$
$\frac{\Delta_c H^\circ}{kJ\ mol^{-1}}$	−286.0	−394.0	−1560.0

The enthalpy of formation of ethane is

(*a*) +54.0 kJ mol^{-1} (*b*) −68.0 kJ mol^{-1}

(*c*) −86.0 kJmol^{-1} (*d*) +97.0 kJ mol^{-1}

Credit:--- Divansh.....

37. While performing a thermodynamics experiment, a student made the following observation.

$HCl + NaOH \rightarrow NaCl + H_2O \ \Delta H = -57.3 \text{ kJ mol}^{-1}$

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O \ \Delta H = -55.3 \text{ kJ mol}^{-1}$

The enthalpy of ionization of CH_3COOH as calculated by the student is ________ kJ mol^{-1}. (Nearest integer)

[25 July, 2022 (Shift-II)]

38. At 298.2 K the relationship between enthalpy of bond dissociation (in kJ mol^{-1}) for hydrogen (EH) and its isotope, deuterium (ED), is best described by:

[25 July, 2021 (Shift-I)]

(a) $E_H = E_D$ (b) $E_H = \frac{1}{2}E_D$

(c) $E_H = 2E_D$ (d) $E_H = E_D - 7.5$

39. When 400 mL of 0.2 M H_2SO_4 solution is mixed with 600 mL of 0.1 M NaOH solution the increase in temperature of the final solution is ________ $\times 10^{-2}$ K. (Round off to the Nearest Integer).

[Use: $H^+(aq) + OH^-(aq) \rightarrow H_2O : \Delta_r H = -57.1 \text{ kJmol}^{-1}$]

Specific heat of $H_2O = 4.18 \text{ JK}^{-1}\text{g}^{-1}$

Density of $H_2O = 1.0 \text{ gcm}^{-3}$

[Assume no change in volume of solution on mixing]

[27 July, 2021 (Shift-II)]

40. Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol^{-1} and 4 kJ mol^{-1}, respectively. The hydration enthalpy of NaCl is: [5 Sept, 2020 (Shift-II)]

(a) 784 kJ mol^{-1} (b) –784 kJ mol^{-1}

(c) 780 kJ mol^{-1} (d) –780 kJ mol^{-1}

41. The standard heat of formation ($\Delta_f H^\circ_{298}$) of ethane (in kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are –1560, –393.5 and –286 kJ/mol respectively is _____.

[7 Jan, 2020 (Shift-II)]

42. An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol^{-1} K^{-1}, the temperature of Al is increased by:

[10 Jan, 2019 (Shift-II)]

(a) $\frac{3}{2}$K (b) 2 K (c) $\frac{2}{3}$K (d) 1 K

43. Given: [12 Jan, 2019 (Shift-II)]

(i) $C(graphite) + O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = x \text{ kJ mol}^{-1}$

(ii) $C(graphite) + \frac{1}{2} O_2(g) \rightarrow CO(g); \Delta_r H^\circ = y \text{ kJ mol}^{-1}$

(iii) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g); \Delta_r H^\circ = z \text{ kJ mol}^{-1}$

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?

(a) $x = y + z$ (b) $z = x + y$

(c) $y = 2z - x$ (d) $x = y - z$

44. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. [JEE Adv 2019]

(a) $\frac{3}{2}O_2(g) \rightarrow O_3(g)$

(b) $\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$

(c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(d) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

SPONTANEITY, ENTROPY, GIBBS ENERGY CHANGE AND EQUILIBRIUM

45. For a certain thermochemical reaction $M \rightarrow N$ at T = 400 K, $\Delta H = 77.2 \text{ kJ mol}^{-1}$, $\Delta S = 122 \text{ JK}^{-1}$, log equilibrium constant (logK) is –______ $\times 10^{-1}$.

[27 Jan, 2024 (Shift-II)]

46. Which of the following is not correct?

[29 Jan, 2024 (Shift-I)]

(a) ΔG is negative for a spontaneous reaction

(b) ΔG is positive for a spontaneous reaction

(c) ΔG is zero for a reversible reaction

(d) ΔG is positive for a non-spontaneous reaction

47. For a certain reaction at 300K, K = 10, then ΔG° for the same reaction is –________ $\times 10^{-1}$ kJ mol^{-1}.

(Given R = 8.314 JK^{-1} mol^{-1}) [01 Feb, 2024 (Shift-II)]

48. For the reaction at 298 K, $2A + B \rightarrow C$, $\Delta H = 400 \text{ kJ mol}^{-1}$ and $\Delta S = 0.2 \text{ kJ mol}^{-1} \text{K}^{-1}$. The reaction will become spontaneous above ________ K. [06 April, 2024 (Shift-II)]

49. When $\Delta H_{vap} = 30$ kJ/mol and $\Delta S_{vap} = 75 \text{ J mol}^{-1} \text{K}^{-1}$, then the temperature of vapour, at one atmosphere is ______ K.

[09 April, 2024 (Shift-II)]

50. Which of the following relations are correct?

(A) $\Delta U = q + p\Delta V$ (B) $\Delta G = \Delta H - T\Delta S$

(C) $\Delta S = \frac{q_{rev}}{T}$ (D) $\Delta H = \Delta U - \Delta n_g RT$

Choose the most appropriate answer from the options given below: [29 Jan, 2023 (Shift-II)]

(a) (C) and (D) only (b) (B) and (C) only

(c) (A) and (B) only (d) (B) and (D) only

51. For independent process at 300 K.

Process	ΔH/kJ mol^{-1}	ΔS/J K^{-1}
A	–25	–80
B	–22	40
C	25	–50
D	22	20

The number of non-spontaneous process from the following is ________.

[24 Jan, 2023 (Shift-I)]

52. Match the List-I with List-II **[27 June, 2022 (Shift-I)]**

	List-I		List-II
A.	Spontaneous process	I.	$\Delta H < 0$
B.	Process with $\Delta P = 0$, $\Delta T = 0$	II.	$\Delta G_{T,P} < 0$
C.	$\Delta H_{reaction}$	III.	Isothermal and Isobaric process
D.	Exothermic Process	IV.	[Bond energies of molecules in reactants] - [Bond energies of product molecules]

Choose the correct answer from the option given below:

(*a*) (A)-(III), (B)-(II), (C)-(IV), (D)-(I)
(*b*) (A)-(II), (B)-(III), (C)-(IV), (D)-(I)
(*c*) (A)-(II), (B)-(III), (C)-(I), (D)-(IV)
(*d*) (A)-(II), (B)-(I), (C)-(III), (D)-(IV)

53. Which of the following relation is not correct? **[28 July, 2022 (Shift-I)]**

(*a*) $\Delta H = \Delta U - P\Delta V$ (*b*) $\Delta U = q + W$
(*c*) $\Delta S_{sys} + \Delta S_{surr} \geq 0$ (*d*) $\Delta G = \Delta H - T\Delta S$

54. Assuming ideal behaviour, the magnitude of log K for the following reaction at 25°C is $x \times 10^{-1}$.

The value of x is ________ (integer answer)

$3HC \equiv CH(g) \rightleftharpoons C_6H_6(l)$

[Given: $\Delta_f G^\circ(HC \equiv CH) = -2.04 \times 10^5\ J\ mol^{-1}$; $\Delta_f G^\circ(C_6H_6) = -1.24 \times 10^5\ J\ mol^{-1}$; $R = 8.314\ JK^{-1}mol^{-1}$]

[24 Feb, 2021 (Shift-II)]

55. Data given for the following reaction is as follows:

$FeO(s) + C_{(graphite)} \longrightarrow Fe(s) + CO(g)$

Substance	$\Delta_f H^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1}K^{-1})
$FeO_{(s)}$	−266.3	57.49
$C_{(graphite)}$	0	5.74
$Fe_{(s)}$	0	27.28
$CO_{(g)}$	−110.5	197.6

The minimum temperature in K at which the reaction becomes spontaneous is ___

(Integer answer) **[27 Aug, 2021 (Shift-II)]**

56. For one mole of an ideal gas, which of these statements must be true? **[4 Sept, 2020 (Shift-I)]**

(A) U and H each depends only on temperature
(B) Compressibility factor z is not equal to 1
(C) $C_{P,m} - C_{V,m} = R$
(D) $dU = C_v dT$ for any process

(*a*) (A), (C) and (D) (*b*) (B), (C) and (D)
(*c*) (A) and (C) (*d*) (C) and (D)

57. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by:

$\Delta_r G^\circ = A - BT$

Where A and B are non – zero constant. Which of the following is TRUE about this reaction?

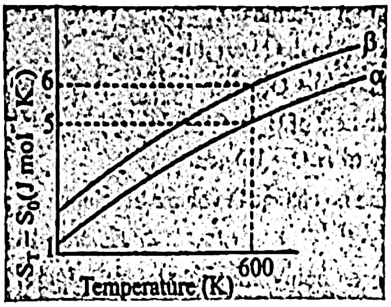
[11 Jan, 2019 (Shift-II)]

(*a*) Endothermic if $A > 0$
(*b*) Exothermic if $A > 0$ and $B < 0$
(*c*) Endothermic if $A < 0$ and $B > 0$
(*d*) Exothermic if $B < 0$

"PARAGRAPH"

The entropy versus temperature plot for phases α and β at 1 bar pressure is given.

S_T and S_0 are entropies of the phases at temperatures T and 0 K, respectively.



The transition temperature for α to β phase change is 600 K and $C_{P,\beta} - C_{P,\alpha} = 1\ J\ mol^{-1}\ K^{-1}$. Assume $(C_{P,\beta} - C_{P,\alpha})$ is independent of temperature in the range of 200 to 700 K. $C_{P,\alpha}$ and $C_{P,\beta}$ are heat capacities of α and β phases, respectively.

58. The value of entropy change, $S_\beta - S_\alpha$ (in J mol^{-1} K^{-1}), at 300 K is _______. **[JEE Adv 2023]**

[Use: ln 2 = 0.69

Given: $S_\beta - S_\alpha = 0$ at 0 K]

59. The value of enthalpy change, $H_\beta - H_\alpha$ (in J mol^{-1}), at 300 K is _______. **[JEE Adv 2023]**

60. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

At 298 K: $\Delta_f H^\circ(SnO_2(s)) = -581.0$ kJ mol^{-1}, $\Delta_f H^\circ(CO_2(g)) = -394.0$ kJ mol^{-1},

$S^\circ(SnO_2(s)) = 56.0$ J K^{-1} mol^{-1}, $S^\circ(Sn(s))$ 52.0 J K^{-1} mol^{-1},

$S^\circ(C(s)) = 0.6$ J K^{-1}mol^{-1}, $S^\circ(CO_2(g)) = 210.0$ J K^{-1} mol^{-1}.

Assume that the enthalpies and the entropies are temperature independent. **[JEE Adv 2020]**

PASSAGE I

Amount of 50 g of a 4 % sodium hydroxide solution and 50 g of a 1.825 % solution of hydrochloric acid were mixed in a heat insulated vessel at a temperature of 20°C. The temperature of the solution obtained in this way increased to 23.4°C. Then 70 g of a 3.5 % solution of sulphuric acid at a temperature of 20°C were added to the above solution.

1. Calculate the number of milli moles of unreacted NaOH. **(Integer Type)**
2. Calculate the final temperature (in °C) of the resulting solution. **(Integer Type)**
3. Determine the amount of a dry residue (in mg) that remains after evaporation of the solution.
   (heat capacity value $c = 4.19\ J\ g^{-1}\ K^{-1}$.)
   Relative atomic masses:
   $A_r(H) = 1; A_r(O) = 16; A_r(Na) = 23; A_r(S) = 32; A_r(Cl) = 35.5.$ **(Integer Type)**

PASSAGE II

Photosynthesis may be summarised by the overall equation:

$$6CO_2(g) + 6H_2O(l) \xrightarrow[\text{chlorophyll}]{\text{light}} C_6H_{12}O_6(s) + 6O_2(g)$$

at 25 °C:

$\Delta H = 2.87 \times 10^6\ J\ mol^{-1}$, $\Delta S = -182\ J\ K^{-1}\ mol^{-1}$.

Imagine that there have been devised electrodes that would allow selective reduction of oxygen to water and oxidation of glucose to carbon dioxide in a galvanic cell, i.e., a reverse process when compared with that of the photosynthetic reaction.

4. What will be the electromotive force (in milli Volt) of the cell in which light energy would be transformed to electric energy by means of the photosynthetic reaction? **(Integer Type)**
5. How many moles of photons with wavelength 500 nm take part in the above reaction? **(Integer Type)**
6. Calculate, what would be the electric power (in W) of a square swimming pool with a side of 10 m containing green algae capable of the photosynthetic reaction if under average illumination a current of 1 mA can be expected from the area of 1 cm². **(Integer Type)**

PASSAGE III

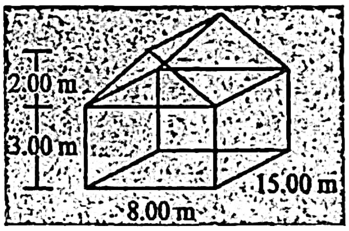
For his 18th birthday party in February, Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition.

Chemical Substance	mol fraction x	$\Delta_f H^\circ$ (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	C_p° (J mol^{-1} K^{-1})
$CO_2(g)$	0.0024	–393.5	213.8	37.1
$N_2(g)$	0.0134	0.0	191.6	29.1
$CH_4(g)$	0.9732	–74.6	186.3	35.7
$C_2H_6(g)$	0.0110	–84.0	229.2	52.5
$H_2O(l)$	-	–285.8	70.0	75.3
$H_2O(g)$	-	–241.8	188.8	33.6
$O_2(g)$	-	0.0	205.2	29.4

The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C).

Assume that all products are gaseous. (Natural gas, methane, and ethane are not ideal gases).

7. Assume that dinitrogen is inert under the chosen conditions. Calculate the value of Gibbs energy (in kJ/mol) under standard conditions (1.013×10^5 Pa, 25.0 °C) for the combustion of reaction I and reaction II as Z and W respectively.
   I) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
   II) $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
   Find the value of Z – W.
   (assuming that all products are gaseous). **(Integer Type)**
8. Calculate the magnitude of combustion energy (in MJ) which is released as thermal energy during the burning of 1.00 m³ of natural gas under standard conditions. **(Integer Type)**
9. Calculate the amount of methane and ethane (in moles) in 1.00 m³ of natural gas as X and Y respectively. Find the value of $\frac{10}{9} \times (X - Y)$. **(Integer Type)**
10. The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00°C and the air temperature in the house (dimensions given in the figure below) is 10.0°C. Assume water density of $\rho = 1.00\ kg\ dm^{-3}$ and air behaving like an ideal gas.



Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0 °C. **(Integer Type)**

11. Calculate the energy (in MJ) which is required to heat the initial amount of air (21.0 % of O_2, 79.0 % of N_2) to 30.0 °C at a pressure of 1.013×10^5 Pa. **(Integer Type)**

PASSAGE IV

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The student may be aware that the acceptable concentration of CO in air is ≤ 5 ppm and the maximum tolerable level is 50 ppm.

The following reactions occur in methane burner:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)\ (I)$$

$$CH_4(g) + 3/2\ O_2(g) \rightarrow CO(g) + 2\,H_2O(g)\ (II)$$

Compound	CH_4	O_2	CO_2	CO	H_2O
ΔH_f^0 (kJ mol^{-1})	–74.9	0	–393.5	–110.5	–241.8
S^0 (J K^{-1}mol^{-1})	186.2	205.0	213.6	197.6	188.7

12. Calculate the equilibrium constant for reaction (I) at T = 1500 K assuming that the values ΔH^0 and ΔS^0 are independent of the temperature in scientific notation as $X \times 10^Z$. Find the value of 10 X – Z. **(Integer Type)**

13. Calculate the equilibrium constant for reaction (II) at T = 1500 K assuming that the values ΔH^0 and ΔS^0 are independent of the temperature in scientific notation as $Y \times 10^W$. Find the value of Y – 10 W. **(Integer Type)**

14. Find the relationship between the mole numbers of oxygen and carbon monoxide at equilibrium (T = 1500 K, p = 1 atm) when air is admitted into the burner in such amount that the mole ratio $CH_4 : O_2$ is 1 : 2. Assume the following volume composition of air: 80 % N_2 and 20 % O_2.
Make the approximation that $n(CH_4) \cong 0$ at equilibrium

15. Calculate the equilibrium mole fraction x of CO in the conditions given in above question. Assume that the mole fraction of CO is very small in comparison with that of CO_2 and consequently, the total number of moles does not appreciably vary during the combustion. Justify this assumption.

16. Repeat the calculations of items 14 and 15 assuming that twice the amount of air (compared to the conditions in question 14) is admitted into the burner (4 mol O_2 : 1 mol CH_4).

17. Calculate the concentrations of CO (expressed as ppm by volume) in the fumes after condensation of water vapour under the conditions of question 14 and 16, assuming that the composition does not change appreciably during the cooling from 1500 K to room temperature and neglecting the contribution of water vapour to the composition of the gas phase.

NUMERICAL TYPE QUESTION

18. The heat of formation of one mole HI (gas) from hydrogen and iodine vapour at 25°C is 33.6kJ/mol. Find the heat of formation (in kJ/mol) at 10°C given that the heat capacities (JK^{-1} mol^{-1}) of hydrogen, iodine vapour and HI vapour are given by the following equations :

Di-hydrogen : $C_p = 27.3 + 0.0071\ T$;
Iodine vapour: $C_p = 27.3 + 0.0160\ T$;
Hydrogen iodide: $C_p = 27.3 + 0.0067\ T$;
where T is the thermodynamic (absolute) temperature.
(Answer upto one decimal place)

MINDFUL LETTER-WRITING

- Write a heartfelt thank-you note to someone who has positively impacted your life. Focus on recalling specific moments that made you feel grateful for them.
- Deliver the letter in person or send it with a small token of appreciation.

ANSWER KEY

CONCEPT APPLICATION

1. (*b*) 2. (*d*) 3. (*d*) 4. (*b*) 5. (*d*) 6. (*a*) 7. (*a*) 8. (*b*) 9. (*a*) 10. (*c*)
11. (*c*) 12. (*c*) 13. (*a*) 14. (*c*) 15. (*d*) 16. (*a*) 17. (*b*) 18. (*c*) 19. (*c*) 20. (*b*)
21. (*d*) 22. (*a*) 23. (*b*) 24. (*a*) 25. (*a*) 26. (*a*) 27. (*b*) 28. (*b*) 29. (*a*) 30. (*d*)
31. (*a*) 32. (*c*) 33. (*d*) 34. (*b*) 35. (*a*) 36. (*b*) 37. (*c*) 38. (*b*) 39. (*b*) 40. (*d*)

SCHOOL LEVEL PROBLEMS

1. (*b*) 2. (*c*) 3. (*a*) 4. (*d*) 5. (*c*) 6. (*b*) 7. (*b*) 8. (*c*) 9. (*c*) 10. (*c*)
11. (*a*) 12. (*c*) 24. (i)-(*a*), (ii)-(*a*), (iii)-(*b*), (iv)-(*c*)

PRARAMBH (TOPICWISE)

1. (*c*) 2. (*c*) 3. (*c*) 4. (*a*) 5. (*c*) 6. (*b*) 7. (*b*) 8. (*a*) 9. (*d*) 10. (*b*)
11. (*b*) 12. (*a*) 13. (*b*) 14. (*d*) 15. (*c*) 16. (*d*) 17. (*b*) 18. (*b*) 19. (*c*) 20. (*c*)
21. (*c*) 22. (*d*) 23. (*d*) 24. (*d*) 25. (*b*) 26. (*d*) 27. (*a*) 28. (*a*) 29. (*c*) 30. (*d*)
31. (*d*) 32. (*d*) 33. (*d*) 34. (*a*) 35. (*a*) 36. (*a*) 37. (*d*) 38. (*b*) 39. (*a*) 40. (*a*)
41. (*c*) 42. (*a*) 43. (*d*) 44. (*a*)

PRABAL (JEE MAIN LEVEL)

1. (*d*) 2. (*b*) 3. (*b*) 4. (*d*) 5. (*d*) 6. (*a*) 7. (*c*) 8. (*c*) 9. (*b*) 10. (*c*)
11. (*c*) 12. (*c*) 13. (*d*) 14. (*c*) 15. (*a*) 16. (*c*) 17. (*b*) 18. (*d*) 19. (*a*) 20. (*b*)
21. (*b*) 22. (*c*) 23. (*b*) 24. (*c*) 25. (*d*) 26. (*c*) 27. (*a*) 28. (*d*) 29. (*a*) 30. (*d*)
31. (*c*) 32. (*a*) 33. (*b*) 34. (*d*) 35. (*a*) 36. (*a*) 37. (*d*) 38. (*b*) 39. (*b*) 40. (*b*)
41. (*b*) 42. (*c*) 43. (*c*) 44. (*a*) 45. (*c*) 46. [7] 47. [4] 48. [3] 49. [43] 50. [501]
51. [100] 52. [32]

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*b*) 2. (*a*) 3. (*c*) 4. (*a*) 5. (*c*) 6. (*a*) 7. (*d*) 8. (*d*) 9. (*c*) 10. (*a*)
11. (*c*) 12. (*c*) 13. (*a*) 14. (*a,b,d*) 15. (*a,b,c*) 16. (*b,d*) 17. (*b,d*) 18. (*b,d*) 19. (*a,b,c*) 20. (*a,b,c*)
21. (*a,b*) 22. (*a,b,c*) 23. (*b*) 24. (*a*) 25. (*d*) 26. (*a*) 27. (*b*) 28. (*d*) 29. (*a*) 30. (*c*)
31. (*a*) 32. (*b*) 33. (*c*) 34. (*d*) 35. (*c*) 36. (*d*) 37. (*a*) 38. (*a*) 39. (a) 40. (*c*)
41. (*d*) 42. (*a*) 43. [4] 44. [6] 45. [1200] 46. [2880] 47. [14] 48. [10] 49. [137] 50. [10]
51. [2924] 52. [1.40] 53. [8.4] 54. [10.2] 55. [7.52]

PYQ's (PAST YEAR QUESTIONS)

1. (*a*) 2. [4] 3. [3] 4. (*a*) 5. [1200] 6. [200] 7. [28721] 8. (d) 9. [200] 10. [274]
11. [55] 12. [150] 13. [0] 14. [8630] 15. [0] 16. [15] 17. [2218] 18. [48] 19. (*a,b,c*) 20. (*a*)
21. [7] 22. (*a,b,d*) 23. [10] 24. [56] 25. [492] 26. [125] 27. (*b*) 28. [150] 29. [6535] 30. [37]
31. [82] 32. (*a*) 33. [610] 34. [1200] 35. (*c*) 36. (*c*) 37. [2] 38. (*d*) 39. [82] 40. (*b*)
41. [192.5] 42. (*c*) 43. (*a*) 44. (*a,b*) 45. [37] 46. (b) 47. [57] 48. [2000] 49. [400] 50. (*b*)
51. [2] 52. (*b*) 53. (*a*) 54. [855] 55. [964] 56. (*a*) 57. (*a*) 58. [0.31] 59. [300] 60. [935]

PW CHALLENGERS

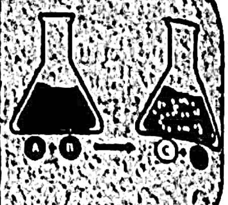
1. [25] 2. [24] 3. [3550] 4. [1240] 5. [12] 6. [1240] 7. [2084] 8. [36] 9. [48] 10. [1318]
11. [12] 12. [19] 13. [1] 14. [$n_{O_2} = 0.5\, n_{CO}$] 15. [7.06×10^{-5}] 16. [7.11×10^{-7}]
17. [86 ppm, 0.8 ppm] 18. [33.6]

Credit:--- Divansh.....

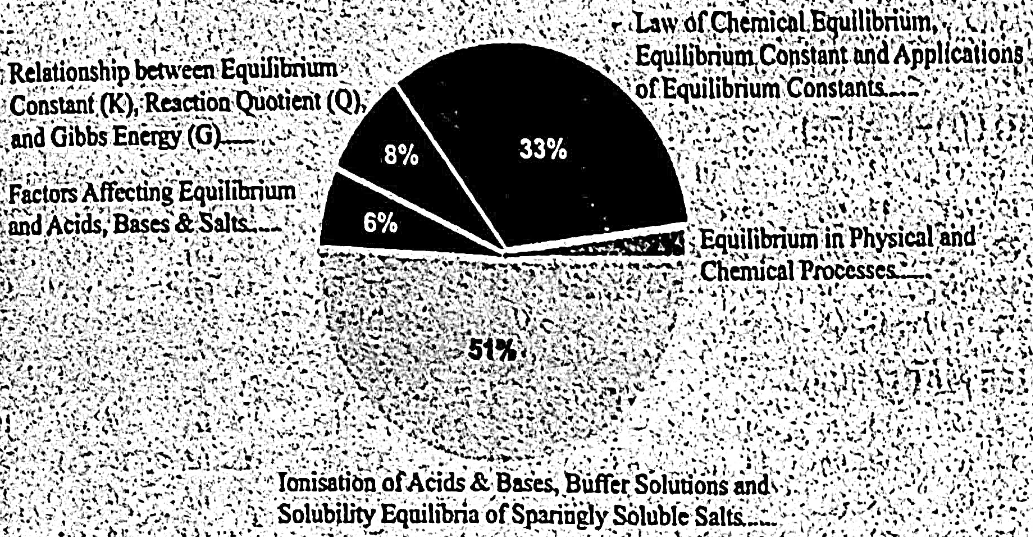
CHAPTER

8

Equilibrium



Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josh?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

INTRODUCTION

The term "equilibrium" in physical sense is defined as the "no change of state of the body". The state of the body can be either the state of rest or the state of uniform motion. Such static equilibrium can be further categorized into stable and unstable equilibriums.

You all must be acquainted with another well known equilibrium, equilibrium between liquid water and its vapour, $H_2O(\lambda) \rightleftharpoons H_2O(g)$. When H_2O (l) is taken in a closed container, some water molecules go into the vapour phase (vaporization process) and simultaneously, water molecules return to the liquid phase (condensation process). Initially, the rate of vaporization is greater than the rate of condensation but after some time the rate of evaporation and the rate of condensation becomes equal. Thus, the number of water molecules leaving and the number of water molecules returning to the liquid phase are equal.

At this stage, both the processes takes place but it seems that the changes are not occurring, as the composition of the system does not change. Such processes in which forward and backward changes are occurring at the same rate are referred as *dynamic equilibrium*. This $H_2O(l) \rightleftharpoons H_2O(g)$ equilibrium involving two phases of the same substance is called *physical equilibrium* because the changes that occur are physical changes.

In this lesson, we will be more concerned with the state of equilibrium attained in chemical reactions. Most of the chemical reactions are reversible in nature (i.e., occurs in both the directions). At the start of a reversible process containing only reactants, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, theoretically the reverse process also begins to take place and reactant molecules are formed from product molecules.

Credit:--- Divansh.....

Types of Chemical Reactions

Irreversible Reactions

The reaction which proceed in one direction only

(*a*) Precipitation reactions e.g.

$NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

(*b*) Neutralization reactions e.g.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$

(*c*) Reactions in open vessels with one of the gaseous product

Reversible Reactions

Reactions which proceed in both the direction. These are possible only in closed vessel e.g.

(*a*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(*b*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Difference between Irreversible and Reversible Reactions

	Irreversible Reactions		Reversible Reactions
1.	The reaction which proceeds in one direction (forward direction) only	1.	The reaction which proceed in both the direction under the same set of experimental conditions
2.	Reactants are almost completely converted into products. Products do not react to form reactants again.	2.	Reactants form products and products also form reactants in backward direction simultaneously. These are possible in closed vessels.
3.	Do not attain equilibrium state.	3.	Attain the equilibrium state and never go to completion.
4.	Such reactions are represented by single arrow (→)	4.	Represented by double arrow ($\rightleftharpoons$) or ($\rightleftharpoons$).
5.	Examples: (*a*) Precipitation reactions e.g. $NaCl(s) + AgNO_3(aq) \rightarrow NaNO_3(aq) + \underset{(s)}{AgCl\downarrow}$ (*b*) Neutralization reactions involving strong acid/strong base e.g. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$ (*c*) Reactions in open vessels. Even a reversible gaseous reaction will become irreversible if it is carried out in open vessel. Example: $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$ $NH_4HS(s) \xrightarrow{\Delta} NH_3(g) + H_2S(g)$	5.	Examples: (*a*) Homogeneous reactions-only one phase is present (*i*) Gaseous phase reactions. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ [Birkeland cyde process (HNO_3)] $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Haber's process) (*ii*) Liquid phase reactions. $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ (*b*) Heterogeneous reactions: More than one phases are present: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

STATE OF CHEMICAL EQUILIBRIUM

State of equilibrium means the factors taking the reaction in forward direction and in the backword direction are balancing each other.

The equilibrium state represents a compromise between two opposing tendencies.

- Tendency to minimise energy.
- Molecules trying to maximise entropy.

In a reversible reaction like-

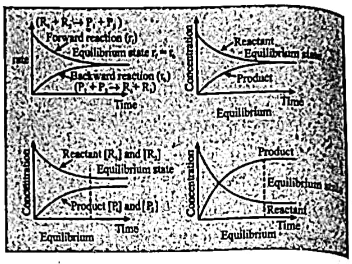
$$\underbrace{R_1 + R_2}_{\text{Reactants}} \rightleftharpoons \underbrace{P_1 + P_2}_{\text{Products}}$$

Consider initially only reactants are present. R_1 and R_2 combine to form P_1 and P_2. As soon as P_1 and P_2 are formed, they start the backward reaction. As concentrations of R_1 and R_2 decrease, rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when both the rates become equal. Such a state is known as "Chemical Equilibrium" or "state of Equilibrium".

At Equilibrium:

(*i*) Rate of forward reaction (r_f) = rate of backward reaction (r_b)

(*ii*) All measurable parameters become constant with respect to time.



Types of Equilibrium on the Basis of Process

Physical Equilibrium
Equilibrium in physical process is called physical equilibrium.
For example phase changes like
$H_2O(l) \rightleftharpoons H_2O(g)$;

Chemical Equilibrium
Equilibrium in chemical process is called chemical equilibrium.
For example
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

Types of Equilibria on the Basis of Physical State

Homogeneous equilibrium;
When all reactants and products are in same phase
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

Heterogeneous equilibrium;
when more than one phase are present
$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
$2Na_2O_2(s) + 2H_2O(l) \rightleftharpoons 4NaOH + O_2(g)$

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

- The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved from both directions.
- Equilibrium is dynamic in nature.
- It means that at microscopic level reaction has not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.
- A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.
- Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc. which may be suitable in a given reaction.
- At equilibrium, free energy change $\Delta G = 0$
- Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc.

- System moves toward an equilibrium state spontaneously even if it is disturbed.

Law of mass action:

- Rate at which a substance reacts ∝ [Active Mass of the substance]^x

Active Mass = Molar concentration (for dilute solution)

It is represented in square brackets i.e. [ ] e.g. [A], $[N_2]$ etc.

- The rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients.

Ex. $aA(g) + bB(g) \rightarrow$ products
Rate of reaction $\alpha\ [A]^a [B]^b$
Rate $= k\,[A]^a [B]^b$,
where k is the rate constant of the reaction.

EQUILIBRIUM CONSTANT (K)

For a general reaction : $aA + bB \rightleftharpoons cC + dD$,
Forward reaction rate $r_f = k_f [A]^a\ [B]^b$,
Backward reaction rate $r_b = k_b [C]^c [D]^d$,
At equilibrium, $r_f = r_b$

$k_f [A]^a_{eq} [B]^b_{eq} = k_b [C]^c_{eq} [D]^d_{eq}$

The concentrations of reactants & products at equilibrium are related by $\dfrac{k_f}{k_b} = K_c = \dfrac{[C]^c_{eq}\ [D]^d_{eq}}{[A]^a_{eq}\ [B]^b_{eq}}$

- **K_c is a constant for given reaction at given temperature and is called the equilibrium constant in terms of concentration.** (Where all the concentrations are at equilibrium and are expressed in moles/litre.)

e.g. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$\Rightarrow \quad K_c = \frac{[PCl_3]_{eq}\ [Cl_2]_{eq}}{[PCl_5]_{eq}}$$

e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\Rightarrow \quad K_c = \frac{[NH_3]^2_{eq}}{[N_2]_{eq}\ [H_2]^3_{eq}}$$

e.g. $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$

$$\Rightarrow \quad K_c = \frac{[HI]_{eq}}{[H_2]^{1/2}_{eq} [I_2]^{1/2}_{eq}}$$

- **$K_p \rightarrow$ Equilibrium constant in terms of partial pressure.** It is defined for the equilibrium reaction which contains gaseous components. If component other than gas is present, its active mass must be one.

e.g. $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

$$K_p = \frac{[P_C]^c_{eq}\ [P_D]^d_{eq}}{[P_A]^a_{eq}\ [P_B]^b_{eq}}$$

where various pressures are the partial pressures of various gaseous substances.

- For pure solids and pure liquids, although they have their own active masses but their concentration remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.

  e.g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

  $K_C = [CO_2],\ K_P = P_{CO_2}$

- K_x → Equilibrium constant in terms of mole fraction of reactants and products.

Train Your Brain

Example 1: Four vessel each of volume V = 10 Litre contains

(a) 16 g $CH_4(g)$ (b) 18 g $H_2O(g)$

(c) 35.5 g $Cl_2(g)$ (d) 44 g $CO_2(g)$

Find the active masses in all the containers.

Sol. (a) $\Rightarrow [CH_4] = \dfrac{16}{16\times10} = 0.1\ M$

(b) $\Rightarrow [H_2O] = \dfrac{18}{18\times10} = 0.1\ M$

(c) $\Rightarrow [Cl_2] = \dfrac{35.5}{71\times10} = 0.05\ M$

(d) $\Rightarrow [CO_2] = \dfrac{44}{44\times10} = 0.1\ M$

Example 2: The equilibrium constant expression for the equilibrium

$2NH_3(g) + 2O_2(g) \rightleftharpoons N_2O(g) + 3H_2O(g)$ is

Sol. $2NH_3(g) + 2O_2(g) \rightleftharpoons N_2O(g) + 3H_2O(g)$

$$K_c = \frac{[N_2O]\times[H_2O]^3}{[NH_3]^2\times[O_2]^2}$$

Example 3: Calculate the expression for K_c and K_p if initially a moles of N_2 and b moles of H_2 is taken for the following reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(P, T, V given)

Sol. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ (\Delta n < 0)$

At	$t = 0$	a	b	0
	$t = t_{eq}$	$(a-x)$	$(b-3x)$	$2x$

$$[N_2] = \frac{a-x}{V},\ [H_2] = \frac{b-3x}{V},\ [NH_3] = \frac{2x}{V}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

Credit:--- Divansh.....

Total no. of moles at equilibrium = a + b – 2x

$$[P_{N_2}] = \frac{(a-x)}{a+b-2x}.P, \quad [P_{H_2}] = \frac{(b-3x)}{a+b-2x}.P,$$

$$[P_{NH_3}] = \frac{(2x).P}{a+b-2x}$$

$$\therefore K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{\left(\frac{2x}{a+b-2x}.P\right)^2}{\left[\left(\frac{a-x}{a+b-2x}\right).P\right]\left[\frac{(b-3x)P}{a+b-2x}\right]^3}$$

$$K_p = \frac{\frac{4x^2.P^2}{(a+b-2x)^2}}{P^4.\frac{(a-x)(b-3x)^3}{(a+b-2x)^4}} = \frac{(a+b-2x)^2.4x^2}{P^2(a-x)(b-3x)^3}$$

Concept Application

1. The decomposition of N_2O_4 to NO_2 was carried out in chloroform at 280°C. At equilibrium, 0.2 mol of N_2O_4 and 2×10^{-3} mole of NO_2 were present in 2L of solution. The equilibrium constant (K_c) for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is
   (*a*) 1.0×10^{-5} (*b*) 2.0×10^{-3}
   (*c*) 2.0×10^{-5} (*d*) 0.01×10^{-5}
2. In a reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, A and B are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium is reached, concentration of C was thrice the concentration of B, Calculate K_C.
   (*a*) 1.2 (*b*) 1.4 (*c*) 1.6 (*d*) 1.8
3. An example of a reversible reaction is:
   (*a*) $Pb(NO_3)_2(aq) + 2NaI(aq) \rightleftharpoons PbI_2(s) + 2NaNO_3(aq)$
   (*b*) $AgNO_3(aq) + HCl(aq) \rightleftharpoons AgCl(s) + HNO_3(aq)$
   (*c*) $2Na(s) + H_2O(l) \rightleftharpoons 2NaOH(aq) + H_2(g)$
   (*d*) $KNO_3(aq) + NaCl(aq) \rightleftharpoons KCl(aq) + NaNO_3(aq)$
4. For the reaction, $A + B \rightleftharpoons 3C$, if 'a' mol/litre of each 'A' & 'B' are taken initially then at equilibrium the incorrect relation is:
   (*a*) $[A] - [B] = 0$ (*b*) $3[B] + [C] = 3a$
   (*c*) $3[A] + [C] = 3a$ (*d*) $[A] + [B] = 3[C]$

- **Relation between K_P & K_C**

$PV = nRT$ or $P = \frac{n}{V}RT$

$P = CRT$ where $C = \frac{n}{V}$

Consider, $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

Credit:--- Divansh.....

$P_C = [C]RT; P_D = [D]RT; P_A = [A]RT; P_B = [B]RT$

$$\Rightarrow K_p = \frac{[C]^c(RT)^c[D]^d(RT)^d}{[A]^a(RT)^a[B]^b(RT)^b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)};$$

$K_p = K_c(RT)^{\Delta n_g}$ Where $\Delta n_g = (c+d)-(a+b)$

[$\Rightarrow \Delta n_g$ = sum of the number of moles of gaseous products –sum of the number of moles of gaseous reactants.]

Δn_g can be positive, negative, zero or even fraction.

e.g., $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$\Delta n_g = 1$ (because there is only one gas component in the products and no gas component in the reactant)

$\Rightarrow K_p = K_c.(RT)$

Key Note

- $K_p = K_x.(P_T)^{\Delta n_g}$
- If $\Delta n_g = 0 \Rightarrow K_p = K_c = K_x$

UNIT OF EQUILIBRIUM CONSTANTS

- Unit of K_p is $(atm)^{\Delta n_g}$
- Unit of K_c is $(mole/L)^{\Delta n_g} = (conc.)^{\Delta n_g}$
- K_x has no units as mole fraction is unitless quantity.

Key Note

- In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.

Train Your Brain

Example 4: The value of K_P for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 50. What is the value of K_C?

(*a*) 30 (*b*) 40 (*c*) 50 (*d*) 70

Sol. As $\Delta n_g = 0$

So, $K_p = K_c(RT)^{\Delta n_g}$

Put $\Delta n_g = 0$

$\Rightarrow \boxed{K_p = K_c}$

So $K_p = 50$

Example 5: The equilibrium constant K_C for the decomposition of PCl_5 is 0.625 mole/lit at 300°C. Then the value of K_P is:

(*a*) 29.40 atm (*b*) 0.0625 atm

(*c*) 6.25 atm (*d*) 0.00625 atm

Sol. $K_c = 0.625$ mole/litre

$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ $\Delta n_g = 1$

$K_p = K_c(RT)$

$K_p = 0.625 \times 0.0821 \times 573$

$= 29.40$ atm

Example 6: The ratio of K_P/K_C for the reaction: $CO(g) + (1/2)O_2(g) \rightleftharpoons CO_2(g)$ is

(*a*) 1.0 (*b*) RT

(*c*) $1/\sqrt{RT}$ (*d*) $(RT)^{1/2}$

Sol. $\Delta n_g = 1 - \frac{1}{2} - 1 = -\frac{1}{2}$

$$\frac{K_p}{K_c} = (RT)^{-1/2} = \frac{1}{\sqrt{RT}}$$

So, $\boxed{\frac{K_p}{K_c} = \frac{1}{\sqrt{RT}}}$

Concept Application

5. For which of the following K_P is less than K_c?

(*a*) $N_2O_4 \rightleftharpoons 2NO_2$ (*b*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(*c*) $H_2 + I_2 \rightleftharpoons 2HI$ (*d*) $CO + H_2O \rightleftharpoons CO_2 + H_2$

6. For homogeneous gas reaction $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$. The equilibrium constant K_c has the unit of-

(*a*) $(concentration)^1$ (*b*) $(concentration)^{-1}$

(*c*) $(concentration)^9$ (*d*) $(concentration)^{10}$

7. The value of K_P for the reaction. $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$ is 0.03 atm at 427°C, when the partial pressure are expressed in atmosphere, then the value of K_C for the same reaction is

(*a*) 5.22×10^{-4} (*b*) 7.34×10^{-4}

(*c*) 3.2×10^{-3} (*d*) 5.43×10^{-5}

CHARACTERISTICS OF EQUILIBRIUM CONSTANT & FACTORS AFFECTING IT

- Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst and direction from which equilibrium is reached.
- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- **Equilibrium constant depends only on the temperature for given reaction.**

It means K_p and K_c will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

- However if temperature is changed,

$$\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right];\ \Delta H = \text{Enthalpy of reaction}$$

If $T_2 > T_1$ then $K_2 > K_1$ provided $\Delta H = +ve$ (endothermic reaction)

If $T_2 > T_1$ then $K_2 < K_1$ if $\Delta H = -ve$ (exothermic reaction)

- If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1.K_2$

$A(g) \rightleftharpoons B(g), K_1$

$B(g) \rightleftharpoons C(g), K_2$

On adding $A(g) \rightleftharpoons C(g); K = K_1.K_2$

- If the reaction having eq. constant K_1 is reversed then resulting equation has eq. constant $\frac{1}{K_1}$

$A(g) + B(g) \rightleftharpoons C(g) + D(g); K_1$

On reversing, $C(g) + D(g) \rightleftharpoons A(g) + B(g); K = \frac{1}{K_1}$

- If a chemical reaction having equilibrium constant K_1 is multiplied by a factor n then the resulting equation has equilibrium constant $K = (K_1)^n$, n can be fraction

eg. $D_2(g) \rightleftharpoons 2A(g); K_1$

Multiplying by $\left(\frac{1}{2}\right)$

$\left(\frac{1}{2}\right)D_2(g) \rightleftharpoons A(g); K = (K_1)^{1/2} = \sqrt{K_1}$

Train Your Brain

Example 7: The value of K_c for the reaction, $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ at a certain temperature is 400 L/mole, calculate the value of equilibrium constant for.

(*i*) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$

(*ii*) $(1/2)N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$

Sol. Equilibrium constant (K_c) for the reaction $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ is

$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 400$$

(*i*) For the reaction $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$,

$$K'_c = \frac{[N_2][O_2]^2}{[NO_2]^2} = \frac{1}{K_c}$$

$$K'_c = \frac{1}{400} = 0.0025 \text{ mole litre}^{-1}$$

(*ii*) For the reaction $(1/2)N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$

$$K''_c = \frac{[NO_2]}{[N_2]^{1/2}[O_2]} = \sqrt{K_c}$$

$$\Rightarrow K''_c = \sqrt{400} = 20 \text{ litre}^{1/2}\text{ mole}^{-1/2}$$

Example 8: For the reaction : $A \rightleftharpoons B$; $K_C = 2$, $B \rightleftharpoons C$; $K_c = 4$, $C \rightleftharpoons D$; $K_c = 6$; K_c for the reaction $A \rightleftharpoons D$.

(*a*) 12 (*b*) 4/5

(*c*) 24 (*d*) 48

Sol. $A \rightleftharpoons B \quad K_{c_1} = 2$ ...(i)

$B \rightleftharpoons C \quad K_{c_2} = 4$ ...(ii)

$C \rightleftharpoons D \quad K_{c_3} = 6$ ...(iii)

$A \rightleftharpoons D \quad K_{c_4}$ ...(iv)

We get $A \rightleftharpoons D$ reaction

by (i) + (ii) + (iii)

So, $K_{c_4} = K_{c_1} \times K_{c_2} \times K_{c_3}$

$K_{c_4} = 2 \times 4 \times 6 = 48$

Example 9: The equilibrium constant for the reaction, $Br_2 \rightleftharpoons 2Br$, at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The reaction is

(*a*) endothermic (*b*) exothermic

(*c*) fast (*d*) slow

Sol. As with increase in temperature, equilibrium constant increases so it is an endothermic process.

Concept Application

8. The equilibrium constant of the reaction $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is $4 \times 10^{-3}\ atm^{-1/2}$. The equilibrium constant of the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ would be:

   (*a*) 250 atm (*b*) 4×10^3 atm

   (*c*) 0.25×10^4 atm (*d*) 6.25×10^4 atm

9. The value of equilibrium constant for a reaction depends on

   (*a*) Temperature (*b*) Pressure

   (*c*) Volume (*d*) Catalytic agent

10. Equilibrium constant for a reaction $A + 2B \rightleftharpoons 2C$ is 40. The equilibrium constant for reaction $2C \rightleftharpoons 2B + A$ is:

    (*a*) $\frac{1}{40}$ (*b*) $\left(\frac{1}{40}\right)^{1/2}$

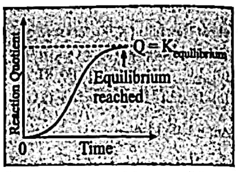
    (*c*) $\left(\frac{1}{40}\right)^{2}$ (*d*) 40

PREDICTING THE DIRECTION OF THE REACTION

Reaction Quotient (Q): At each point in a reaction, we can write a ratio of concentration terms having the same form as of the equilibrium constant expression. This ratio is called the reaction quotient denoted by symbol Q.

It helps in predicting the direction of a reaction.

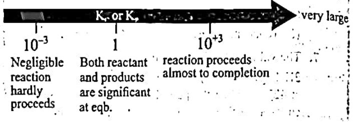
The expression $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ at any time during reaction is called reaction quotient. The concentrations [C], [D], [A], [B] are not necessarily at equilibrium.



- The reaction quotient is a variable quantity with time.
- It helps in predicting the direction of a reaction.
- If $Q > K_c$ reaction will proceed in backward direction until equilibrium is reached.
- If $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
- If $Q = K_c$ Reaction is at equilibrium.

PREDICTING THE EXTENT OF THE REACTION

$$K = \frac{[Product]_{eq}}{[Reactant]_{eq}}$$


Kc or Kp
very large
10⁻³
1
10⁺³
Negligible reaction hardly proceeds
Both reactant and products are significant at eqb.
reaction proceeds almost to completion

Case-I: If K is large ($K > 10^3$) then product concentration is very very larger than the reactant at eqb. ([Product] >> [Reactant]) In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

Case-II: If K is very small ($K < 10^{-3}$)

[Product] << [Reactant] at eqb

In this case, the reaction is reactant favourable.

Ex. The K_P values for three reactions are 10^{-5}, 20 and 300 then what will be the correct order of the percentage composition of the products?

Sol. Since K_p order is $10^{-5} < 20 < 300$ so the percentage composition of products will be greatest for $K_p = 300$.

- **Calculating equilibrium concentrations:** The concentration of various reactants and products can be calculated using the equilibrium constant and the initial concentrations.

Train Your Brain

Example 10: For the reaction $NOBr(g) \rightleftharpoons NO(g) + \frac{1}{2}Br_2(g)$ $K_P = 0.15$ atm at 90°C. If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will Br_2 be consumed or formed?

Sol. $Q_P = \frac{\left[P_{Br_2}\right]^{1/2}[P_{NO}]}{[P_{NOBr}]} = \frac{[0.2]^{1/2}[0.4]}{[0.50]} = 0.36$

$K_P = 0.15$

$\therefore Q_P > K_P$

Hence, reaction will shift in backward direction

$\therefore Br_2$ will be consumed

Example 11: Assuming that the system is at equilibrium, which of the following reactions goes most nearly to 100% completion at equilibrium?

(*a*) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ $K_C = 6.5 \times 10^{-23}$

(*b*) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ $K_C = 0.176$

(*c*) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $K_C = 1 \times 10^{16}$

(*d*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_C = 54.5$

Sol. Greater value of K_c, means reaction mostly goes to completion.

Concept Application

11. The equilibrium constant for the reaction; $N_2(g) + O_2(g) \rightleftharpoons 2NO_{(g)}$ is 4×10^{-4} at 200 K. In the presence of a catalyst the equilibrium is attained 10 times faster. Therefore the equilibrium constant in presence of catalyst at 200 K is

    (*a*) 4×10^{-3} (*b*) 4×10^{-4}

    (*c*) 4×10^{-5} (*d*) None of these

EQUATION INVOLVING IONS

Equilibrium involving ions always take place in aqueous medium.

Ex. $Ag^+(aq.) + Cl^-(aq.) \rightleftharpoons AgCl(s)$

$$K_c = \frac{1}{[Ag^+][Cl^-]}$$

Homogeneous liquid system: e.g., Formation of ethyl acetate: The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Equilibrium

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

e.g., $H_2O(l) \rightleftharpoons H_2O(g)_{eq}$

$K_P = \left(P_{H_2O(g)}\right)_{eq}$, $K_C = [H_2O\ (g)]_{eq}$

DEGREE OF DISSOCIATION (α) AND VAPOR DENSITY

It is the fraction of one mole of substance dissociated into the products.

So, α = no. of moles dissociated / initial no. of moles taken

= fraction of moles dissociated out of 1 mole.

Key Note

- **% dissociation = $\alpha \times 100$**

Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5 dissociated then $\alpha = \frac{2}{5} = 0.4$

Let 1 mole of gas A_n dissociates to give n moles of A as follows-

$$\begin{array}{lccl} & A_n(g) & \rightleftharpoons & nA(g) \\ t=0 & a & & 0 \\ t=t_{eq} & a-x & & n.x \quad \Rightarrow \quad \alpha = \frac{x}{a} \Rightarrow x = a\alpha. \end{array}$$

Total number of moles $= a - a\alpha + na\alpha$

$= [1 + (n-1)\alpha]a$

Train Your Brain

Example 12: Calculate the degree of dissociation and K_P for the following reaction.

$$\begin{array}{lcccc} & PCl_5(g) & \rightleftharpoons PCl_3(g) & + & Cl_2(g) \\ t=0 & a & 0 & & 0 \\ t=t & a-x & x & & x \end{array}$$

Since for a mole, x moles are dissociated

Sol. $\because$ For 1 mole, $\frac{x}{a}$ moles $= \alpha$ are dissociated

$\therefore x = a\alpha$

$$\begin{array}{lccc} & PCl_5(g) & \rightleftharpoons PCl_3(g) + & Cl_2(g) \\ \because \text{At } t=t_{eq}; & a-a\alpha & a\alpha & a\alpha \end{array}$$

Total no. of moles at equilibrium $= a + a\alpha = a(1+\alpha)$

$$P_{PCl_5} = \frac{a(1-\alpha)P}{a(1+\alpha)}; P_{PCl_3} = \frac{a\alpha\ .P}{a(1+\alpha)} = P_{Cl_2}$$

$$K_p = \frac{\left\{\left(\frac{\alpha P}{1+\alpha}\right)\right\}^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

$$\boxed{K_p = \frac{\alpha^2\ .P}{1-\alpha^2}\ \text{(Remember)}}$$

Example 13: For the reaction $H_2 + I_2 \rightleftharpoons 2HI$

The value of equilibrium constant is 9.0. The degree of dissociation of HI will be

(*a*) 2 (*b*) 2/5

(*c*) 5/2 (*d*) 1/2

Sol. (*b*) Equilibrium constant of the reaction

$H_2 + I_2 \rightleftharpoons 2HI$ is 9.0

So the equilibrium constant for the dissociation of HI i.e. $2HI \rightleftharpoons H_2 + I_2$ will be 1/9.

$$\begin{array}{ccc} 2HI & \rightleftharpoons H_2 & + \; I_2 \\ 1 & 0 & 0 \\ 1-x & \frac{x}{2} & \frac{x}{2} \end{array}$$

$$K_c = \frac{\frac{x}{2}\times\frac{x}{2}}{(1-x)(1-x)}$$

$$\frac{1}{9} = \frac{x^2}{2\times 2(1-x)^2};\ \frac{1}{3} = \frac{x}{2(1-x)}$$

or $2-2x = 3x$; $5x = 2$; $x = 2/5$

Concept Application

12. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, N_2 & H_2 were taken in the molar ratio of 1:3. Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be

(*a*) P/3 (*b*) P/6

(*c*) P/4 (*d*) P/8

13. For reaction; $A(g) + B(g) \rightleftharpoons AB(g)$, we start with 2 moles of A and B each. At equilibrium 0.8 moles of AB is formed. Then how much of A changes to AB.

(*a*) 20% (*b*) 40%

(*c*) 60% (*d*) 4%

14. At 444°C, the equilibrium constant K for the reaction $2AB(g) \rightleftharpoons A_2(g) + B_2(g)$ is $\frac{1}{64}$. The degree of dissociation of AB will be

(*a*) 10% (*b*) 20 %

(*c*) 30% (*d*) 50%

15. For the reaction: $N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$; total pressure = P, degree of dissociation = 50%. Then K_p would be –

(*a*) 3P (*b*) 2P

(*c*) $\frac{P}{3}$ (*d*) $\frac{P}{2}$

Degree of Dissociation in Terms of Vapour Density or Molar Mass

Calculation of Degree of dissociation from vapour density:

Ex. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$\alpha = \frac{D_T - D_0}{D_0} \text{ or } \frac{D-d}{d}$$

Where: D_T or D = Principal or theoretical vapour density

D_0 or d = Observed or practical vapour density at eqb.

α = Degree of dissociation

$$\boxed{\text{Vapour density} = \frac{\text{Molecular weight}}{2}}$$

$$\text{V.D.} \propto \text{molar mass} \propto \frac{1}{\text{no. of moles}}$$

$$\begin{array}{lcc} \text{Initial moles} & A(g) & \rightleftharpoons nB(g) \\ & 1 & 0 \\ \text{moles at eqb} & (1-\alpha) & (n\alpha) \end{array}$$

$$\Rightarrow \frac{D_T}{D_0} = \frac{n_0}{n_T} = \frac{1-\alpha+n\alpha}{1} = 1+(n-1)\alpha$$

So for a general reversible reaction $n_1A \rightleftharpoons n_2B + n_3C$

$$\boxed{\alpha = \frac{n_1}{\Delta n}\left(\frac{D_T - D_0}{D_0}\right)}$$

When

(*i*) $\Delta n > 0$ then $D_T > D_0$

(*ii*) $\Delta n = 0$ then $D_T = D_0$

(*iii*) $\Delta n < 0$ then $D_T < D_0$

Train Your Brain

Example 14: Vapour density of the equilibrium mixture of the reaction

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is 50. The extent of dissociation of $SO_2Cl_2(g)$ is

(*a*) 33.33 %

(*b*) 35.0 %

(*c*) 30.0 %

(*d*) 66.67 %

Sol. (*b*) $\alpha = \frac{D_T - D_0}{D_0(n-1)}$

or $\alpha = \frac{67.5-50}{50(2-1)} = 0.35$

Concept Application

16. The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2. The percentage dissociation of N_2O_4 at the final temperature is;

(*a*) 88 (*b*) 60 (*c*) 40 (*d*) 70

17. An unknown compound A dissociates at 500°C to give products as follows:

$A(g) \rightleftharpoons B(g) + C(g) + D(g)$

Vapour density of the equilibrium mixture is 50 when it dissociates to the extent to 10%. What will be the molecular weight of Compound A?

(*a*) 120 (*b*) 130 (*c*) 134 (*d*) 140

EXTERNAL FACTORS AFFECTING EQUILIBRIUM (LE CHATELIER'S PRINCIPLE)

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of external change applied and the equilibrium is re-established again under new conditions.

EFFECT OF CONCENTRATION

- If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g. In the following example.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

- If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction.
- If concentration of product is increased then reaction shifts in the backward direction.

Key Note

- The addition of any solid component does not affect the equilibrium.

EFFECT OF PRESSURE

- On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

$P \propto$ no. of moles

(*i*) For $\Delta n_g = 0 \rightarrow$ No. effect

(*ii*) For $\Delta n_g > 0$, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_P = \frac{(X_{PCl_3}P).(X_{Cl_2}P)}{(X_{PCl_5}.P)}$$

$\Rightarrow Q_P \propto P$ [X = mole fraction]

$P\downarrow; Q_P\downarrow \Rightarrow$ Forward shift

$P\uparrow; Q_P\uparrow \Rightarrow$ Backward shift

(*iii*) For $\Delta ng < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_P = \frac{[(X_{NH_3})P)]^2}{[(X_{N_2}).P][(X_{H_2})P]^3} \Rightarrow Q_P \propto \frac{1}{P^2}$$

$P\uparrow; Q_P\downarrow \Rightarrow$ Forward shift; $P\downarrow; Q_P\uparrow \Rightarrow$ Backward shift

EFFECT OF VOLUME

- If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- If volume is increased then, for

$\Delta n_g > 0$ reaction will shift in the forward direction

$\Delta n_g < 0$ reaction will shift in the backward direction

$\Delta n_g = 0$ reaction will not shift.

eg. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (No effect) of pressure or volume change.

- **Effect of catalyst:** Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the equilibrium will be attained faster i.e time taken to reach the equilibrium is less. But eqb. composition is unaffected.
- **Effect of inert gas addition**

(*i*) **At constant volume:** Inert gas addition has no effect at constant volume

(*ii*) **At constant pressure:** If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

(*i*) $\Delta n_g > 0$, reaction will shift in the forward direction

(*ii*) $\Delta n_g < 0$, reaction will shift in the backward direction

(*iii*) $\Delta n_g = 0$, no effect

- **Effect of temperature**

(*i*) **Exothermic reaction:** The reaction in which heat is evolved

$A(g) + B(g) \rightleftharpoons C(g) + D(g) + \text{Heat}; \Delta H = -ve$

eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

$T\uparrow \Rightarrow K'$ will decrease

$\Rightarrow$ Reaction will shift in backward direction.

$T\downarrow \Rightarrow K$ will increase

$\Rightarrow$ Reaction will shift in forward direction.

(*ii*) **Endothermic reaction:**

$A(g) + B(g) \rightleftharpoons C(g) + D(g) - \text{Heat}; \Delta H = +ve$

$T\uparrow \Rightarrow K\uparrow \Rightarrow$ Forward shift;

$T\downarrow \Rightarrow K\downarrow \Rightarrow$ Backward shift

Credit:--- Divansh.....

Train Your Brain

Example 15: Consider the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; in closed container at equilibrium. What would be the effect of addition of $CaCO_3$ on the equilibrium concentration of CO_2?

(*a*) Increases

(*b*) Decreases

(*c*) Remains unaffected

(*d*) Data is not sufficient to predict it

Sol. (*c*) Remains unaffected as $CaCO_3$ is solid and there is no effect of adding solid on equilibrium.

Example 16: In the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + X$ cal most favourable condition of temperature and pressure for greater yield of SO_3 are-

(*a*) Low temperature and low pressure

(*b*) High temperature and low pressure

(*c*) High temperature and high pressure

(*d*) Low temperature and high pressure

Sol. (*d*) As reaction is exothermic so it is favoured at low temperature condition.

As $\Delta n_g < 0$ so SO_3 formation is favourable at high pressure condition.

Concept Application

18. For the gas phase reaction
$C_2H_4 + H_2 \rightleftharpoons C_2H_6$, $\Delta H = -32.7$kcal/mole carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by:

(*a*) Increasing the temperature

(*b*) Increasing concentration of H_2

(*c*) Decreasing temperature

(*d*) Increasing pressure

19. On adding inert gas to the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at constant pressure. The degree of dissociation will–

(*a*) Remain unchanged (*b*) Decrease

(*c*) Increase (*d*) None of these

20. What will happen upon adding inert gas to the following reaction
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
at equilibrium at constant volume?

(*a*) N_2 and H_2 are formed in abundance

(*b*) N_2, H_2 and NH_3 will have the same molar concentration

(*c*) The production of ammonia increases

(*d*) No change in the equilibrium

21. Which among the following conditions would lead to increase of yield of the product in the following equilibrium?
$3A_{(g)} + B_{(g)} \rightleftharpoons 4C(g) + \text{heat}$

(*a*) Increase in pressure

(*b*) Increase in volume

(*c*) Increase in temperature

(*d*) Decrease in temperature

THERMODYNAMICS OF EQUILIBRIUM

For a general reaction, $mA + nB \rightleftharpoons pC + qD$,

ΔG is given by:

$\Delta G = \Delta G° + 2.303\ RT \log_{10}Q$

where ΔG = Gibb's Free energy change

$\Delta G°$ = Standard Gibb's Free energy change

Q = reaction quotient

Since, at equilibrium, Q = K

Here K is thermodynamic equilibrium constant replacing K_c or K_p

$K = \dfrac{(a_C)^p (a_D)^q}{(a_A)^m (a_B)^n}$; Here a_X denotes the activity of X.

In fact, 'a_x' is the ratio of the activity of substance at equilibrium and its activity in standard condition. That is why it is unitless and K is also unitless.

Key Note

(*i*) Thermodynamic equilibrium constant is unitless since activity is unitless.

(*ii*) For pure solids & pure liquids, activity is unity.

(*iii*) For gases (ideal behaviour), the activity is its partial pressure (in atm).

(*iv*) For components in solution, activity is molar concentration.

At equilibrium, $\Delta G = 0$

$\Rightarrow \quad \Delta G° = -2.303\ RT \log_{10}K$

Now since, $\Delta G° = \Delta H° - T\Delta S°$

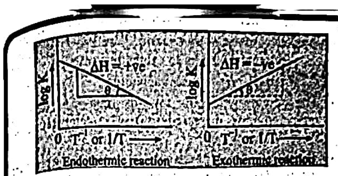
where $\Delta H°$ = Standard enthalpy change of the reaction

$\Delta S°$ = Standard entropy change

$\Rightarrow \quad -2.303\ RT \log_{10}K = \Delta H° - T\Delta S°$

$$\Rightarrow \quad \log_{10}K = -\frac{\Delta H°}{2.303}\cdot\frac{1}{RT} + \frac{\Delta S°}{2.303R}$$

If plot of ln k vs $\frac{1}{T}$ is plotted then it is a straight line with slope $= -\frac{\Delta H°}{R}$, and intercept $= \frac{\Delta S°}{R}$



$$\text{Slope} = \frac{-\Delta H°}{2.303R} = \tan\theta\ ;\ \text{y intercept} = \frac{\Delta S°}{2.303R}$$

If at temperature T_1, equilibrium constant is K_1 and at T_2, it is K_2 then;

$$\log_{10}K_1 = \frac{-\Delta H°}{2.303R}\cdot\frac{1}{T_1} + \frac{\Delta S°}{2.303R} \quad ...(i)$$

$$\log_{10}K_2 = \frac{-\Delta H°}{2.303R}\cdot\frac{1}{T_2} + \frac{\Delta S°}{2.303R} \quad ...(ii)$$

[Assuming $\Delta H°$ and $\Delta S°$ remains constant in this temperature range.]

Subtract eq. (*ii*) from (*i*) we get

$$\textbf{Vant Hoff equation: } \log\left(\frac{K_1}{K_2}\right) = \frac{\Delta H°}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- ΔH should be substituted with sign.
- Unit of $\Delta H/T$ and gas constant R should be same.
- For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature
- For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

Condition for Spontaneity: $\Delta G < 0$ for spontaneous process or reaction.

Since, $\Delta G = \Delta H - T\Delta S$

$\Rightarrow \Delta H - T\Delta S < 0 \Rightarrow T > \Delta H/\Delta S$ for spontaneity

- $\Delta G > 0$ for non-spontaneous process or reaction
- $\Delta G = 0$ for equilibrium

Ex. From the following data:

(*i*) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)\ K_{2000K} = 4.4$

(*ii*) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)\ K_{2000K} = 5.31 \times 10^{-10}$

(*iii*) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)\ K_{1000K} = 2.24 \times 10^{22}$

State whether the reaction (*iii*) is exothermic or endothermic?

Sol. Equation (*iii*) = – [2 × (*i*) + (*ii*)]

$$\therefore K_{2000(iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$\because T\uparrow K\downarrow \Rightarrow$ reaction is exothermic.

Train Your Brain

Example 17: For the reaction,

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$ at 298K, the values of $\Delta H°$ and $\Delta S°$ are –29.8 kcal/mol and –0.1 kcal K^{-1} respectively. The values of $\Delta G°$ and equilibrium constant K_c are:

(*a*) 1, 2 respectively (*b*) 0, 2 respectively

(*c*) 0, 1 respectively (*d*) 0, 0 respectively

Sol. (*d*) $\Delta G° = \Delta H° - T\,\Delta S°$

$\Delta H° = -29.8 \times 10^3$ Cal

$\Delta S° = -0.1 \times 10^3$ Cal

$\Delta G° = -29.8 \times 10^3 - [-0.1 \times 10^3 \times 298]$

$\Delta G° = -29800 + 29800$

$\Delta G° = 0$

$\Delta G° = -2.303\ RT \log_{10} K_c$

$$\log_{10} K_c = \frac{-\Delta G°}{2.303 \times RT} = \frac{0}{2.303 \times 8.314 \times 298}$$

$\log_{10} K_c = 0$ $K_c = 1$

Example 18: For the reaction,

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, the values of $\Delta H°$ and $\Delta S°$ at 298K are 77.2 kJ mol^{-1} and 122 JK^{-1} mol^{-1} respectively. The standard equilibrium constant at the same temperature is:

(*a*) 0.692×10^{-8} (*b*) 6.92×10^{-8}

(*c*) 69.2×10^{-8} (*d*) 692×10^{-8}

Sol. (*b*) $\Delta G° = \Delta H° - T\Delta S° = 77.2 \times 10^3 - 298 \times 122$

$= 77.2 \times 10^3 - 36356 = 40844$

$\Delta G° = -2.303\ RT \log_{10} K_c$

$40844 = -2.303 \times 2477.57 \log_{10} K_c$

$= -5705.84 \log_{10} K_c$

$= \log K_c = -7.16$

$K_c = 6.92 \times 10^{-8}$

Concept Application

22. Van't Hoff's equation giving the effect of temperature on chemical equilibrium may be represented as -

(*a*) $\frac{d}{dT} \ln K_p = \frac{\Delta H°}{RT^2}$ (*b*) $\frac{d}{dT} \ln K_c = \frac{\Delta H° T^2}{R}$

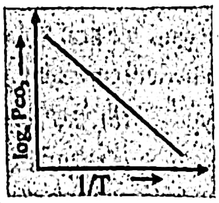
(*c*) $\frac{d}{dT} \ln K_p = \frac{\Delta H° T^2}{R}$ (*d*) $\frac{d}{dT} \ln K_p = \frac{RT^2}{\Delta H°}$

Credit:--- Divansh.....

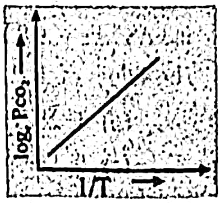
23. For the chemical equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

ΔH_f° can be determined from which one of the following plots?

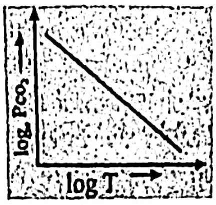
(*a*)



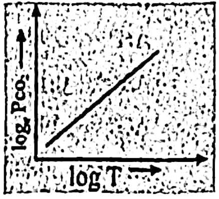
(*b*)



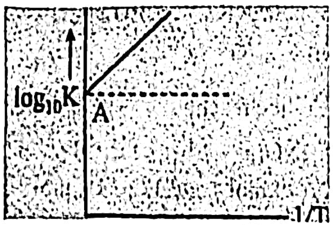
(*c*)



(*d*)



24. Variation of $\log_{10}K$ with $\frac{1}{T}$ is shown by the following graph in which straight line is at 45°, hence ΔH° is:



(*a*) + 4.606 cal/mol
(*b*) – 4.606 cal/mol
(*c*) 2cal/mol
(*d*) –2 cal/mol

25. Q_p represent the reaction quotient of a gas phase reaction and K_p represent the equilibrium constant of the same gas phase reaction. For the non-spontaneous reaction:

(*a*) $\frac{Q_p}{K_p} > 1$
(*b*) $\frac{Q_p}{K_p} < 1$
(*c*) $\frac{Q_p}{K_p} = 1$
(*d*) $Q_pK_p = 1$

PHYSICAL EQUILIBRIUM

Physical reaction: Those reaction in which change in only and only state of substance takes place without any chemical change is called physical reaction.

(*a*) **Ice-water system (melting of ice):** Melting of ice is accompanied by absorption of heat (endothermic) and decrease in volume

Ice(s)	$\rightleftharpoons$	water(*l*)
1gram (1.09 mL)		1gram (1.01 mL)

Hence both increase of temperature and pressure will favour the melting of ice into water.

(*b*) **Water-water vapour system (Vapourisation of water):**

Vapourisation of water is an endothermic and condensation of vapour into water is an exothermic reaction:

$$\text{Water}(l) \rightleftharpoons \text{Water vapour}(g)$$

- The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.
- The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.
- Thus favourable conditions for conversion of water into vapour are high temperature and low pressure.

(*c*) **Solubility of gases:**

$$\underset{\text{(Solute)}}{\text{Gas}(g)} + \underset{\text{(Solvent)}}{\text{Water}(l)} \rightleftharpoons \underset{\text{(Solution)}}{\text{Aqueous solution}(l)}$$

- Effect of pressure → Solubility of gases which dissolve in a solvents increases with a decrease in volume, and with increasing pressure.

IONIC EQUILIBRIUM

Introduction

Ionic Equilibrium: Weak electrolytes are partially ionised in aqueous solution and an equilibrium is situated between the ionised and unionised electrolyte. This type of equilibrium is known as ionic equilibrium.

Let us consider an acid HA which when dissolved in water, an equilibrium will be setup between ionised and unionised acid molecule as below -

$$HA + H_2O \rightleftharpoons H^+ + A^-$$

All the substances can be classified into

Non electrolytic substances	Electrolytic Substances
❖ Does not dissociate into ions on dissolving in solvent like water.	❖ Will dissociate on dissolving in water into ions.
❖ Solution will not conduct electricity eg. C_6H_6, diethyl ether	❖ Solution will conduct electricity eg. all acids, bases, all salts Hg_2Cl_2 dissolve but dissociate negligibly.

Electrolytic Substances

Strong electrolyte	Weak electrolyte
❖ α = unity (100% ionisation) Eg. Strong acids (generally $HClO_4$, HI, HBr, HCl, H_2SO_4, HNO_3), strong bases (generally (NaOH, KOH, RbOH, CsOH and $Ba(OH)_2$) all type of salts (SASB, SAWB, WASB, or WAWB).	❖ α <<< 10% or $\alpha < 0.1$ (generally valid if $K_{eq} < 10^{-3}$) electrolytes not 100% dissociated Eg. weak acids (CH_3COOH, HCN), weak bases (NH_3, $Zn(OH)_2$)

Key Note

The value of α degree of dissociation of electrolysis depends

(*a*) **Nature of electrolyte:** Strong electrolyte dissociate completely where as weak electrolytes dissociate partially.

(*b*) **Nature of solvent:** A solvent having high value of dielectric constant will favour dissociation.

(*c*) **Dilution:** For weak electrolytes, degree of dissociation will increases on dilution (Ostwald's dilution law)

(*d*) **Temperature:** On increasing temperature generally degree of dissociation increases.

(*e*) **Presence of other solute:** When a substance is present, it may effect the solubility of the another solute. Generally presence of common ion suppresses degree of dissociation of weak electrolyte.

OSTWALD'S DILUTION LAW

This law deals with the application of the law of mass action to the equilibrium between the ions and unionized molecules in aqueous solutions of weak binary electrolytes such as acetic acid, propanoic acid, HCN, NH_4OH, etc.

Consider a dilute solution of a weak binary electrolyte AB containing c moles in 1 litre. At any given temperature, there will be equilibrium between the unionized molecules of AB and the ions A^+ and B^-. Let 'α' be the degree of dissociation of AB at equilibrium.

	AB	⇌	A^+	+	B^-
Initial conc.	c		0		0
Conc. at. equilibrium	$c(1-\alpha)$		$c\alpha$		$c\alpha$

Then according to the law of mass action, the equilibrium constant K_{eq} will be given by

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

This expression "$K_{eq} = \frac{\alpha^2 c}{1-\alpha}$" is called *Ostwald's dilution law.*

K_{eq} is called the dissociation (or ionization) constant of the weak electrolyte. α has a very small value for a weak electrolyte and is therefore negligible in comparison with unity.

$$\therefore 1-\alpha \approx 1. \qquad \therefore K_{eq} = \alpha^2 c$$

$$\alpha = \sqrt{\frac{K_{eq}}{c}} \quad ; \quad \alpha \propto \sqrt{V}$$

This law is valid only for weak electrolytes that too in dilute solutions. It is not applicable for strong electrolytes.

ACIDS, BASES AND SALTS

Arrhenius Concept

Arrhenius Acid: Substance which gives H^+ ion on dissolving in water (H^+ donor)

eg. HNO_3, $HClO_4$, HCl, HI, HBr, H_2SO_4, H_3PO_4 etc.

Types of Acids

Mono basic acid	Di basic acid	Tri basic acid
❖ Gives single H^+ per molecule e.g HA HNO_3, $HClO_4$, HCl, H_3PO_2	❖ Gives two H^+ per molecule e.g H_2A H_2SO_4, H_3PO_3	❖ Gives three H^+ per molecule e.g H_3A H_3PO_4

- ❖ H_3BO_3 is not Arrhenius acid.
- ❖ H^+ ion in water is extremely hydrated (in form of H_3O^+, $H_5O_2^+$, $H_7O_3^+$) and has high charge density.

Arrhenius base: Any substance which releases OH^- (hydroxyl) ion in water (OH^- ion donor)

Types of Base

Mono acidic base	Di acidic base	Tri acidic base
❖ Gives single OH^- per molecule e.g CsOH RbOH, NH_4OH	❖ Gives two OH^- per molecule e.g $Ba(OH)_2$ $Ca(OH)_2$	❖ Gives three OH^- per molecule e.g $Fe(OH)_3$

- ❖ OH^- ion also in hydrated form of $H_3O_2^-$, $H_7O_4^-$, $H_5O_3^-$
- ❖ First group elements (except Li.) form strong bases.

Bronsted - Lowery Concept: (Conjugate Acid - Base Concept) (Protonic Concept)

Acid: Substances which donate H^+ are Bronsted Lowery acids (H^+ donor)

Base: Substances which accept H^+ are Bronsted Lowery bases (H^+ acceptor)

Conjugate acid - base pairs

In a typical acid base reaction

$$HX + B \rightleftharpoons X^- + HB^+$$

$$\underset{\text{acid}}{HX} + \underbrace{\underset{\text{base}}{B} \rightleftharpoons \underset{\substack{\text{Conjugate}\\ \text{acid}}}{HB^+}}_{\substack{\text{Conjugate}\\ \text{pair}}} + \underset{\substack{\text{Conjugate}\\ \text{base}}}{X^-}$$

Acid		Base		Conjugate Acid		Conjugate Base
HCl	+	H_2O	⇌	H_3O^+	+	Cl^-
HSO_4^-	+	NH_3	⇌	NH_4^+	+	SO_4^{2-}
$[Fe(H_2O)_6]^{3+}$	+	H_2O	⇌	H_3O^+	+	$[Fe(H_2O)_5(OH)]^{2+}$

- ❖ **Conjugate acid – base pair differ only by one proton**
- ❖ Strong acid will have weaker conjugate base and vise versa
- ❖ Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

e.g. Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	H_2O	H_3O^+
HSO_4^-	SO_4^{2-}	RNH_2	RNH_3^+
H_2O	OH^-		

Amphoteric (amphiprotic) Species: Substances which can act as acid as well as base are known as amphoteric species e.g., HCO_3^-, HSO_4^- etc.

$$HCl + \underset{\text{base}}{H_2O} \rightleftharpoons H_3O^+ + Cl^-$$

$$NH_3 + \underset{\text{acid}}{H_2O} \rightleftharpoons NH_4^+ + OH^-$$

Lewis Acids and Bases

According to Lewis concept of acids and bases, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.

An acid base reaction is the sharing of an electron pair with an acid by a base. This process is simply defined as coordination or neutralisation.

Lewis Acids

(*a*) Generally cations act as Lewis acids i.e., H^+, Ag^+, Fe^{2+} etc.

(*b*) Electron deficient molecules in which octet of central atom is not complete.

e.g. $AlCl_3$, BF_3, BCl_3, $BeCl_2$ etc.

(*c*) Molecules whose central atom can show expansion of octet due to availability of empty d-orbital.

e.g., SiX_4, GeX_4, SnX_4, PX_3, PF_5, SF_4. $TeCl_4$. SeF_4 etc.

Lewis Bases

(*a*) Neutral species having at least one or more lone pair of electrons available at central atom

eg. $:PH_3$, $:NH_3$. $R\ddot{\underset{\cdot\cdot}{O}}H$, $R—\ddot{N}H_2$ etc.

(*b*) Negatively charged species or anions e.g., Cl^- CN, OH, X^-, NH_2^-, SH^- etc.

(*c*) Molecules having multiple bond between atoms of dissimilar electronegativities

e.g., CO_2, SO_2 etc.

Note: All bronsted bases are also Lewis bases but all bronsted acids are not Lewis adds.

Strong and Weak Acids and Bases

Acids and Bases are classified as strong or weak.

A **strong acid** is an acid that ionizes completely in water

e.g., $HCl(aq) + H_2O(l) \rightarrow H_3O^+ (aq) + Cl^- (aq.)$

$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+ (aq) + NO_3^- (aq.)$

A **weak acid** is an acid that is only partially ionized in water

$CH_3COOH (aq) + H_2O(l) \rightleftharpoons CH_3COO^- (aq) + H_3O^+ (aq)$

$HCN (aq) + H_2O(l) \rightleftharpoons CN^- (aq) + H_3O^+ (aq)$

A **strong base** is a base that ionizes completely in water

$KOH(s) \xrightarrow{H_2O} K^+ (aq) + OH^- (aq)$

$Ca(OH)_2(aq) \rightarrow Ca^{+2} (aq) + 2OH^- (aq)$

A **weak base** is a base which is partially ionized in water

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+ (aq) + OH^- (aq)$

Train Your Brain

Example 19:

(*a*) Write conjugate acids of
SO_4^{2-}, RNH_2, NH_2^-, $C_2H_5O\,C_2H_5$, F^-

(*b*) Write conjugate base of
HNO_2, OH^-, H_2CO_3, $HClO_4$.

(*c*) Write conjugate acids and conjugate base of following amphoteric species.
HS^-, NH_3, C_2H_5OH, H_2O

Sol. (*a*) HSO_4^-, RNH_3^+, NH_3, $(C_2H_5)_2OH^+$, HF

(*b*) NO_2^-, O^{2-}, HCO_3^-, ClO_4^-

(*c*) Conjugate acids: H_2S, NH_4^+, $C_2H_5OH_2^+$, H_3O^+
Conjugate base: S^{2-}, NH_2^-, $C_2H_5O^-$, OH^-

Example 20: The conjugate acid of HPO_4^{2-} is

(*a*) H_3PO_4 (*b*) PO_4^{3-}
(*c*) $H_2PO_4^-$ (*d*) H_3O^+

Sol. $HPO_4^{2-} + H^+ \longrightarrow H_2PO_4^-$

Example 21: In the reaction $SnCl_2 + 2Cl^- \rightarrow SnCl_4$, $SnCl_2$ is regarded as

(*a*) Lewis acid (*b*) Lewis base
(*c*) Neutral salt (*d*) Basic salt

Sol. $SnCl_2$ is a lewis acid because $SnCl_2$ is a electron acceptor.

Concept Application

26. According to Bronsted concept, the acids in the following reaction
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ are
(*a*) NH_3 and NH_4^+ (*b*) H_2O and OH^-
(*c*) H_2O and NH_4^+ (*d*) NH_3 and OH^-

27. According to the Lewis acid-base concept-
(*a*) Species in which the central atom has complete octet cannot act as an acid
(*b*) Negatively charged ions are acids
(*c*) Molecule in which a central atom has vacant d-orbitals available can act as an acid
(*d*) All positively charged ions are bases

28. Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using Bronsted and Lowry concept?
(*a*) $NH_3 + CH_3COOH \rightleftharpoons CH_3COO^- + NH_4^+$
(*b*) $H_2O + CH_3COOH \rightleftharpoons CH_3COO^- + H_3O^+$
(*c*) $4NH_3 + Cu^{2+} \rightleftharpoons [Cu(NH_3)_4]^{2+}$
(*d*) $HCl + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + Cl^-$

Auto-ionisation of [illegible]

- **Amphoteric (amphiprotic) Acid/base nature:** Water acts as an acid as well as base according to Arrhenius and Bronsted-Lowry theory but according to Lewis concept it can be generally taken as base.

In pure water $[H^+] = [OH^-]$ so it is Neutral.

- **Molar concentration/Molarity of water:**

$$\text{Molarity} = \text{No. of moles/litre} = \frac{1000\text{gm / litre}}{18\text{gm / mole}}$$

$$= 55.55 \text{ mole/litre} = 55.55 \text{ M (density} = 1 \text{ gm/cc)}$$

- **Ionic product of water : According to Arrhenius concept**
$H_2O \rightleftharpoons H^+ + OH^-$ so, ionic product of water,
$K_w = [H^+][OH^-] = 10^{-14}$ at 25°C (experimental)

- Dissociation of water, is endothermic, so on increasing temperature $K_{eq.}$ or (K_w) increases. i.e., the ionisation of water increases with increase in temperature and finally the concentration of H^+ and OH^- ion increases.

Values of K_W at various temperature:

Temperature (°C)	Value of K_W
(1) 25° C	1×10^{-14} (Room temp.)
(2) 90	1×10^{-12}

Now **$pH = -\log[H^+] = 7$ and $pOH = -\log[OH^-] = 7$** for water at 25°C (experimental)

$$\left.\begin{array}{lll} pH = 7 = pOH & \Rightarrow & \text{neutral} \\ pH < 7 \text{ or } pOH > 7 & \Rightarrow & \text{acidic} \\ pH > 7 \text{ or } pOH < & \Rightarrow & \text{Basic} \end{array}\right\} \text{at } 25°C$$

- Ionic product of water is always a constant value whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

- **Degree of dissociation of water:**
$H_2O \rightleftharpoons H^+ + OH^-$

$$\Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{total no.of moles initially taken}}$$

$$= \frac{10^{-7}}{55.55} = 18\text{x}10^{-10} \text{ or } 1.8\text{x}10^{-7}\%$$

ACIDITY AND pH SCALE

- Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.

  So greater the tendency to give H^+, more will be the acidic strength of the substance.

- Basic strength means the tendency of a base to give OH^- ions in water.

  So greater the tendency to give OH^- ions, more will be basic strength of the substance.

- The concentration of H^+ ions is written in a simplified form introduced by Sorenson known as pH scale.

pH of solution may be defined as negative logarithm of hydronium ion concentration.

$$pH = -\log[H_3O^+];\ [H_3O^+] = 10^{-pH}$$

$$pH = \log\frac{1}{[H_3O^+]}$$

Similarly, we can define pOH as $pOH = -\log[OH^-]$, $[OH^-] = 10^{-pOH}$. The pH range at 25°C is taken as 0 to 14.

Relation between pH & pOH

$pH = -\log[H_3O^+]$
$pOH = -\log[OH^-]$
$[H_3O^+][OH^-] = K_w = 10^{-14}$ at 25°C
$\log[H_3O^+] + \log[OH^-] = \log K_w = \log 10^{-14} = -14$
$\boxed{pH + pOH = pK_w = 14}$ at 298 K.

Ionization Constants of Weak Acids and Weak Bases

The dissociation of weak acids or weak bases in water can be represented as an equilibrium process eg.

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
$NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

In general, If a weak acid is represented by HA, its dissociation in water can be represented by the equilibrium.

$HA + H_2O \rightleftharpoons A^-(aq) + H_3O^+(aq)$

Applying the law of chemical equilibrium, the expression for equilibrium constant will be

$$K = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

As H_2O is solvent, its concentration is large and remains almost constant. $K(H_2O) = K_a$ is called dissociation constant of the acid Thus,

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Knowing the value of the dissociation constant of the acid (K_a) and the concentration (c) of the weak acid HA. The concentration of H_3O^+ or $H^+(aq)$ in the solution can be calculated as follows

$$\begin{array}{llll} & HA + H_2O \rightleftharpoons & H_3O^+ & + A^- \\ \text{Initial concentration} & c & 0 & 0 \\ \text{Conc. at eqm.} & (c - c\alpha) & \alpha c & \alpha c \end{array}$$

(Here α is degree of ionisation)

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{\alpha c \times \alpha c}{c(1-\alpha)} = \frac{\alpha^2 c^2}{c(1-\alpha)}$$

Hence, for α <<< 1

$K_a = \alpha^2 c$

$$\boxed{\alpha = \left(\frac{K_a}{C}\right)^{1/2}}$$

$$\boxed{\alpha = (K_a \times V)^{1/2}}$$

Here, V is the volume of the solution in litres containing 1 mole of the electrolyte, $c = \frac{1}{V}$.

In case of a weak electrolyte, at a given temperature, the degree of ionisation is inversely proportional to the square root of the molar concentration or directly proportional to square root of the volume of the solution which contains one mole electrolyte.

This is called **Ostwald's dilution law.**

Similarly the dissociation of a weak base in water can be represented by the equilibrium

$BOH \rightleftharpoons B^+(aq) + OH^-(aq)$

The dissociation constant of the weak base, represented by K_b, will be given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

	$BOH \rightleftharpoons$	$B^+ +$	OH^-
Initial concentration	c	0	0
Concentration at equilibrium	$c(1-\alpha)$	αc	αc

$$\text{Now, } K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{\alpha c \times \alpha c}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

For a weak electrolyte, if α is very small, it can be neglected

$$\therefore \boxed{K_b = \alpha^2 c}$$

Knowing the ionization constant. K_a of an acid and K_b of a base and its initial concentration c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionisation of the acid and base and the pH of the solution

Degree of ionisation for acid (α)

$$= \sqrt{\frac{K_a}{c}} \text{ or } \left(\frac{K_a}{c}\right)^{1/2} \text{ and } c\alpha = [H_3O^+]$$

Degree of ionisation for base (α)

$$= \sqrt{\frac{K_b}{c}} \text{ or } \left(\frac{K_b}{c}\right)^{1/2} \text{ and } c\alpha = [OH^-]$$

Factors Affecting Acidic Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid mainly depends upon two factors i.e., strength and polarity of the H–A bond.

Weaker the H–A bond, more easily it gets dissociated to give H^+ ion and hence, stronger is the acid. Similarly, greater the polarity of the H–A bond i.e., larger the electronegativity difference between the atoms H and A, more easily the bond breaks and hence, greater is the acidic strength.

For elements in the same group of periodic table, the bond strength dominates over the polar nature. Thus, down the group, as size of the atoms increases, bond strength decreases and hence, acidic strength increases. For example, for the element of group-17.

$$\xrightarrow[\text{Acidic strength increases}]{HF << HCl << HBr << HI}$$

Similarly, for the elements of group-16, acidic strength increases as:

$H_2O < H_2S < H_2Se < H_2Te$

For the elements along the same period, however the polarity of the H-A bond decides the acidic strength. With increase in the electronegativity of A the polarity of the bond increases and hence the acidic strength also increases. For example

$$\xrightarrow[\text{Acidic strength increases, electronegativity increases, polarity increases}]{CH_4 < NH_3 < H_2O < HF}$$

Common Ion Effect in the Ionization of Acids and Bases

We know that a weak electrolyte is dissociated to small extent in solution and there is an equilibrium between the undissociated electrolyte and the ions formed in solution. If we add a strong electrolyte, having an ion common with the weak electrolyte, then the dissociation of the weak electrolyte gets further suppressed or decreased.

"The suppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion is called common ion effect."

For example: Ionization of acetic acid (CH_3COOH) and effect of addition of a small amount of acetate ion.

$$CH_3COOH(aq) \rightleftharpoons \boxed{CH_3COO^-(aq)} + H^+(aq)$$

$$CH_3COONa(aq) \longrightarrow \boxed{CH_3COO^-(aq)} + Na^+(aq)$$

Common ion

Due to the presence of common $CH_3COO^-(aq)$ ions, the equilibrium will be shifted to the left according to Le Chatelier's principle.

In order to evaluate the pH of the solution resulting on addition of 0.05 M acetate ion to 0.05 M acetic acid solution we shall consider the acetic acid dissociation equilibrium once again.

	$CH_3COOH(aq) \rightleftharpoons$	$CH_3COO^- +$	$H^+(aq)$
Initial concentration	0.05M	0.05M	0
Equilibrium Concentration	0.05–x	(0.05+x)	x

Here α is the extent of ionization of acetic acid

$$\text{Now, } K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

For a weak electrolyte, $x << 0.05$

Hence. $(0.05 + x) \approx (0.05 - x) \approx 0.05$

$$\text{Thus, } [H^+] = \frac{K_a \times 0.05}{0.05}$$

$[H^+] = K_a = 1.8 \times 10^{-5}$ M

$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$

Credit:--- Divansh.....

RELATIONSHIP BETWEEN pK_a AND pK_b OF CAB PAIR

K_a = Ionization constant of weak acid

K_b = Ionization constant of conjugate base

$HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad ...(i)$$

$A^- + H_2O \rightleftharpoons OH^- + HA$

$$K_b = \frac{[OH^-][HA]}{[A^-]} \quad ...(ii)$$

Multiplying equation (*i*) & (*ii*)

$K_a \times K_b = [H^+][OH^-] = K_w$

i.e., $K_a \times K_b = K_w$

$\therefore \log K_a + \log K_b = \log K_w$

$\boxed{pK_a + pK_b = pK_w}$

pH CALCULATIONS OF DIFFERENT TYPES OF SOLUTIONS

(*a*) **Strong acid Solution:**

(*i*) If concentration is greater than 10^{-6} M

In this case H^+ ions coming from water can be neglected, so $[H^+]$ = normality of strong acid solution.

(*ii*) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected,

So $[H^+]$ = normality of strong acid + H^+ ions coming from water in presence of this strong acid

Ex: Calculate pH of 10^{-8} M HCl solution.

Sol. $H_2O \rightleftharpoons H^+ + OH^-$

$\qquad\qquad 10^{-8} + x \qquad x$

$K_w = [H^+][OH^-]$

$10^{-14} = x(x \times 10^{-8})$

$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4\times10^{-14}}}{2}$$

$$= \frac{-10^{-8} + 10^{-7}\sqrt{4 + \frac{1}{100}}}{2}$$

$$= \frac{(\sqrt{401} - 1)10^{-8}}{2}$$

$= 0.95 \times 10^{-7}$

$[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$M

pH = 7 – log 1.05 ≈ 6.98

Key Note

- For 10^{-9} M HCl pH ≈ 7
- For 10^{-12} M HCl pH ≈ 7

(*b*) **Strong base Solution:** Calculate the $[OH^-]$ which will be equal to normality of the strong base solution and then use $K_W = [H^+] \times [OH^-] = 10^{-14}$, to calculate $[H^+]$.

Ex: Calculate pH of 10^{-7} M of NaOH solution.

Sol. $[OH^-]$ from NaOH = 10^{-7} M

$[OH^-]$ from water = $x \lesssim 10^{-7}$ M

(due to common ion effect)

$H_2O \rightleftharpoons OH^- + H^+$

$\qquad (x + 10^{-7}) \qquad x$

$K_w = [H^+][OH^-] = 10^{-14} = x(x + 10^{-7})$

$x^2 + 10^{-7}x - 10^{-14} = 0$

$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7}$ M $= [H^+]$

pH = 7.21 $\quad (\sqrt{5} = 2.236)$

(*c*) **pH of mixture of two strong acids:** If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2, then

eqv. of H^+ ions from I - solution = N_1V_1

eqv. of H^+ ions from II - solution = N_2V_2

If final normality is N and final volume is V, then

$NV = N_1V_1 + N_2V_2$

$$[H^+] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

(*d*) **pH of mixture of two strong bases:** Similar to above calculation

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \;\&\; [H^+] = \frac{10^{-14}}{[OH^-]}$$

(*e*) **pH of mixture of a strong acid and a strong base:**

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic depending on which component has been taken in excess.
- If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution of normality N_2, then
- Number of eq. of H^+ ions from I-solution = N_1V_1
- Number of eq. of OH^- ions from II-solution = N_2V_2

If $N_1V_1 > N_2N_2$

$$[H^+] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

solution will be acidic in nature

If $N_2V_2 > N_1N_1$

$$[OH^-] = N = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

solution will be basic in nature

$$[H^+] = \frac{10^{-14}}{[OH^-]}$$

Credit:--- Divansh.....

Train Your Brain

Example 22: Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

Sol.	HCl	$+ NaOH \rightarrow$	$NaCl +$	H_2O
Meq. before reaction	$100 \times 0.1 = 10$	$9.9 \times 1 = 9.9$	0	0
Meq. after reaction	0.1	0	9.9	9.9

$$\therefore [H^+] \text{ left from HCl} = \frac{0.1}{109.9} = 9.099 \times 10^{-4} \text{ M}$$

$$\therefore pH = -\log H^+ = -\log (9.099 \times 10^{-4})$$

$$pH = 3.04$$

Example 23: The pH of a solution obtained by mixing 50 ml of 0.4 N HCl and 50 ml of 0.2 N NaOH is

(*a*) $-\log 2$
(*b*) $-\log 0.2$
(*c*) 1.0
(*d*) 2.0

Sol. (*c*) $[H^+] = \dfrac{(50 \times 0.4) - (50 \times 0.2)}{100} = \dfrac{10}{100} = 0.1$

$$pH = -\log[H^+] = 1$$

Example 24: Calculate pH of mixture of (400ml, $\frac{1}{200}$ M Ba(OH)$_2$) + (400ml, $\frac{1}{50}$ M HCl) + (200ml of Water)

Sol. $[H^+] = \dfrac{\left(400 \times \frac{1}{50}\right) - \left(400 \times \frac{1}{200} \times 2\right)}{1000} = 4 \times 10^{-3}$ M,

so $pH = 3 - 2 \log 2 = 2.4$

Concept Application

29. When 100 ml $Ca(OH)_2$ solution of 0.01 M is diluted with water, the pH of the resulting solution changes to 12. Volume of water added is–

(*a*) 10 ml
(*b*) 50 ml
(*c*) 100 ml
(*d*) 200 ml

30. Which of the following have largest pH?

(*a*) $\frac{M}{10}$ HCl
(*b*) $\frac{M}{100}$ HCl
(*c*) $\frac{M}{10}$ NaOH
(*d*) $\frac{M}{100}$ NaOH

31. Solution X has pH = 2 and solution Y has pH = 5 which one of the following is correct ?

(*a*) Solution X is twice as acidic as Y
(*b*) Solution Y is twice as acidic as X
(*c*) Solution X is 1000 times more acidic than Y
(*d*) Solution Y is 1000 times more acidic than X

32. 20 ml of 0.5 N HCl and 35 ml of 0.1 N NaOH are mixed. The resulting solution will

(*a*) be basic

(*b*) be neutral

(*c*) turn methyl orange red

(*d*) turn phenolphthalein solution pink

(*f*) pH of a weak acid (monoprotic) Solution:

- Weak acid does not dissociate 100% therefore we have to calculate the percentage dissociation using K_a (dissociation constant) of the acid.

$$\begin{array}{llll} & HA & \rightleftharpoons H^+ + A^- & \\ t=0 & C & 0 & 0 \\ t=t_{eq} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$K_a=\frac{[H^+][A^-]}{[HA]}=\frac{C\alpha^2}{1-\alpha}$$

If $\alpha<<1 \Rightarrow (1-\alpha)\approx 1 \quad \Rightarrow K_a\approx C\alpha^2$

$$\Rightarrow \alpha=\sqrt{\frac{K_a}{C}} \text{ (is valid if } \alpha<0.1 \text{ or } 10\%)$$

$$[H^+]=C\alpha=C\sqrt{\frac{K_a}{C}}=\sqrt{K_a\times C}$$

$$\Rightarrow \text{So pH}=\frac{1}{2}(pK_a-\log C)$$

on increasing dilution

$\Rightarrow C\downarrow \Rightarrow \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

Train Your Brain

Example 25: Calculate pH of

(*a*) 10^{-1} M CH_3COOH (*b*) 10^{-3} M CH_3COOH,

(*c*) 10^{-6} M CH_3COOH Take $K_a=2\times10^{-5}$.

Sol. (*a*)

$$\Rightarrow \alpha=\sqrt{\frac{K_a}{C}}=\sqrt{\frac{2\times10^{-5}}{10^{-1}}}=\sqrt{2\times10^{-4}}\ (\alpha<<0.1)$$

So, $[H^+]=10^{-1}\times\sqrt{2}\times10^{-2}\Rightarrow pH=3-\frac{1}{2}\log 2=2.85$

$$(b)\quad \alpha=\sqrt{\frac{K_a}{C}}=\sqrt{\frac{2\times10^{-5}}{10^{-3}}}=\sqrt{2\times10^{-2}}\ (\alpha>0.1)$$

So we have to do the exact calculations

$$K_a=\frac{C\alpha^2}{1-\alpha}\Rightarrow 2\times10^{-5}=\frac{10^{-3}\times\alpha^2}{1-\alpha}\Rightarrow \alpha=13.14\%$$

$[H^+]=10^{-3}\times0.1314=1.314\times10^{-4}\Rightarrow pH=4-\log(1.314)\approx3.9$ Ans.

(*c*) If approximation is used then,

$$\alpha=\sqrt{\frac{2\times10^{-5}}{10^{-6}}}=\sqrt{20}>1,$$

so we have to do the exact calculation,

$$2\times10^{-5}=10^{-6}\ \frac{\alpha^2}{1-\alpha}$$

$\Rightarrow \alpha\approx0.95$ or 95%

$[H^+]=0.95\times10^{-6}=9.5\times10^{-7}$

$\Rightarrow$ pH = 7 – log (9.5) = 6.022

Example 26: The pH of 0.5 M aqueous solution of HF $(K_a=2\times10^{-4})$ is-

(*a*) 2 (*b*) 4 (*c*) 6 (*d*) 10

Sol. (*a*) $K_a=C\alpha^2$

$2\times10^{-4}=0.5\alpha^2$

$\boxed{\alpha=2\times10^{-2}}$

$[H^+]=C\alpha=0.5\times2\times10^{-2}=10^{-2}$

$pH=-\log[H^+]=-\log[10^{-2}]=2\log10=2$

Example 27: A monoprotic acid in a 0.1 M solution ionizes to 0.001%. Its ionization constant is:

(*a*) 1.0×10^{-3} (*b*) 1.0×10^{-6}

(*c*) 1.0×10^{-8} (*d*) 1.0×10^{-11}

Sol. (*d*) $K_a=C\alpha^2$

$$K_a=0.1\times\left(\frac{0.001}{100}\right)^2=1\times10^{-11}$$

Concept Application

33. The pH of a 0.1 M aqueous solutions of a weak acid (HA) is 4. what is its degree of dissociation?

(*a*) 1% (*b*) 0.1% (*c*) 50% (*d*) 25%

34. For two weak acids A and B, the ratio of their percent ionization is 4 : 9. The ratio of their K_a would be–

(*a*) 4 : 9 (*b*) 2 : 3 (*c*) 16 : 81 (*d*) 3 : 2

35. Phenoxide ion $(C_6H_5O^-)$ is a weak base, with $K_b=7.7\times10^{-5}$. Calculate the pH of a 0.20 M solution of $C_6H_5O^-$

(*a*) 11.6 (*b*) 3.9×10^{-3}

(*c*) 9.2 (*d*) 8.9

(*g*) pH of a mixture of weak acid (monoprotic) and a strong acid Solution:

- Weak acid and Strong acid both will contribute H^+ ion.
- For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

If [SA] = C_1 and [WA] = C_2, then $[H^+]$ from SA = C_1, the weak acid will dissociate as follows.

$$\begin{array}{llll} HA & \rightleftharpoons & H^+ + & A^- \\ C_2 & & 0 & 0 \\ C_2(1-\alpha) & & C_2\alpha+C_1 & C_2\alpha \end{array}$$

$$K_a=\frac{(C_2\alpha+C_1)C_2\alpha}{C_2(1-\alpha)}\qquad(\alpha<<1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

$K_a=(C_2\alpha+C_1)\alpha$

Total H^+ ion concentration = $C_1+C_2\alpha$

- If the total $[H^+]$ from the acid is greater than 10^{-6} M, then contribution from the water can be neglected at 25°C temperature, if not then we have to take $[H^+]$ from the water also.

(*h*) pH of a mixture of two weak acid (both monoprotic) solutions:

- Both acids will dissociate partially.
- Let the acid are HA_1 & HA_2 and their concentrations in the mixture are C_1 & C_2 respectively, then

$$\begin{array}{llll} & HA_1 & \rightleftharpoons H^+ + & A_1^- \\ t=0 & C_1 & 0 & 0 \\ \text{At eq.} & C_1(1-\alpha_1) & C_1\alpha_1+C_2\alpha_2 & C_1\alpha_1 \\ & HA_2 & \rightleftharpoons H^+ + & A_2^- \\ t=0 & C_2 & 0 & 0 \\ \text{At eq.} & C_2(1-\alpha_2) & C_2\alpha_2+C_1\alpha_1 & C_2\alpha_2 \end{array}$$

$$K_{a1}=\frac{C_1\alpha_1(C_1\alpha_1+C_2\alpha_2)}{C_1(1-\alpha_1)}\ K_{a2}=\frac{(C_2\alpha_2+C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

(Since α_1, α_2 both are small in comparison to unity)

$K_{a1}=(C_1\alpha_1+C_2\alpha_2)\alpha_1;K_{a2}=(C_1\alpha_1+C_2\alpha_2)\alpha_2$

$$\Rightarrow\frac{K_{a1}}{K_{a2}}=\frac{\alpha_1}{\alpha_2}$$

$$[H^+]=C_1\alpha_1+C_2\alpha_2$$

$$=\frac{C_1K_{a1}}{\sqrt{C_1K_{a1}+C_2K_{a2}}}+\frac{C_2K_{a2}}{\sqrt{C_1K_{a1}+C_2K_{a2}}}$$

$$\Rightarrow[H^+]=\sqrt{C_1K_{a1}+C_2K_{a2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected. So, $[H^+]=C_1\alpha_1+C_2\alpha_2\approx C_1\alpha_1$

Train Your Brain

Example 28: Calculate pH of solution obtained by mixing equal volume of 0.02 M HOCl & 0.2 M CH_3COOH solutions. Given that K_{a_1} (HOCl) = 2×10^{-4}, K_{a_2} (CH_3COOH) = 2×10^{-5}. Also calculate $[OH^-]$, $[OCl^-]$, $[CH_3COO^-]$ at equilibrium.

Sol. Volume of final solution become double.

So concentration become half

$C_1 = 0.01$ M, $\quad C_2 = 0.1$ M

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

$$= \sqrt{2\times10^{-4}\times0.01 + 2\times10^{-5}\times0.1}$$

$$= \sqrt{2\times10^{-6} + 2\times10^{-6}} = 2\times10^{-3}\text{ M}$$

pH = 3 – log2 = 2.7

$$\begin{array}{cccc} HOCl & \rightleftharpoons & H^+ & + \; OCl^- \\ C_1(1-\alpha_1) & & C_1\alpha_1 + C_2\alpha_2 & C_1\alpha_1 \\ CH_3COOH & \rightleftharpoons & H^+ & + \; CH_3COO^- \\ C_2(1-\alpha_2) & & C_1\alpha_1 + C_2\alpha_2 & C_2\alpha_2 \end{array}$$

$$\alpha_1 = \frac{2\times10^{-4}}{2\times10^{-3}} = 0.1; \quad \alpha_2 = \frac{2\times10^{-5}}{2\times10^{-3}} = 0.01$$

$[OCl^-] = C_1\alpha_1 \qquad [CH_3COO^-] = C_2\alpha_2$

$= 0.01 \times 10^{-1} \qquad = 0.1 \times 10^{-2}$

$= 1 \times 10^{-3}$ M $\qquad = 1 \times 10^{-3}$ M

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2\times10^{-3}} = 5 \times 10^{-12}\text{ M}$$

Example 29: A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a1} and K_{a2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Sol. $H_2S \rightleftharpoons H^+ + HS^-$; $K_{a1} = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}$; $K_{a2} = 1.3\times10^{-13}$

$HCl \rightarrow H^+ + Cl^-$

Due to common ion effect, the dissociation of H_2S is suppressed and the $[H^+]$ in solution is mainly due to HCl.

$$\therefore K_{a1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$\Rightarrow 10^{-7} = \frac{[0.3][HS^-]}{[0.1]} \quad [\therefore [H^+] \text{ from HCl} = 0.3]$$

$$\therefore [HS^-] = \frac{10^{-7}\times0.1}{0.3} = 3.3 \times 10^{-8}\text{ M}$$

$$\text{Further } K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$\Rightarrow 1.3 \times 10^{-13} = \frac{[0.3][S^{2-}]}{3.3\times10^{-8}}$$

$$\therefore [S^{2-}] = \frac{1.3\times10^{-13}\times3.3\times10^{-8}}{0.3} = 1.43 \times 10^{-20}\text{ M}$$

Concept Application

36. For 10^{-2} M H_3PO_3 solution which of the following relations is correct?

(*a*) $[H_3PO_3] + [H_2PO_3^-] + [HPO_3^{2-}] + [PO_3^{2-}] = 10^{-2}$

(*b*) $[H_3PO_3] + [H_2PO_3^-] + [HPO_3^{2-}] = 10^{-2}$

(*c*) $[H_2PO_3] + [HPO_3^-] + [PO_3^{3-}] = 10^{-2}$

(*d*) $[H_3PO_3] + [H_2PO_3^-] + 2[HPO_3^{2-}] = 10^{-2}$

37. The ratio of acid strength of HOCN and HCN is about (Given K_a of HOCN = 1.2×10^{-4} and K_a of HCN = 4.2×10^{-10})

(*a*) 534 : 1 (*b*) 1 : 548

(*c*) 2.86×10^5 : 1 (*d*) 2.86×10^4 : 1

38. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} & 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be

(*a*) 5.0×10^{-5} (*b*) 5.0×10^{15}

(*c*) 5.0×10^{-15} (*d*) 0.2×10^5

SALTS

Species formed by the reaction of neutralization of acid and base is called as salt.

Simple Salts

These salts formed by the neutralisation process, are of three types.

(*a*) **Normal Salt:** These salts are formed by the neutralization reaction of simple acid and simple base, like - NaCl, NH_4Cl, CH_3COONa, KNO_3 etc.

(*b*) **Acidic Salt:** It is formed by the incomplete neutralization reaction of acid with the base and gives proton in aqueous solution. Like - $NaHCO_3$, $NaHSO_4$, Na_2HPO_4

eg. $H_2SO_4 + NaOH \rightarrow NaHSO_4$

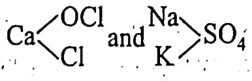
(*c*) **Basic salt:** Salt which is formed by the incomplete neutralization reaction of base with acid and gives OH^- ion in aqueous solution. Like- Zn(OH)Cl, Mg(OH)Cl, $Fe(OH)_2Cl$ etc.

eg. $\underset{1\text{mol}}{Ca(OH)_2} + HCl \rightarrow \underset{\text{Basic salt}}{Ca(OH)Cl}$

eg. $Mg(OH)_2 + \underset{1\text{mol}}{HNO_3} \rightarrow \underset{\text{Basic salt}}{Mg(OH)NO_3}$

eg. $Al(OH)_3 + \underset{1\text{mol}}{HCl} \rightarrow Al(OH)_2Cl \rightarrow \underset{\text{Basic salt}}{Al(OH)Cl_2}$

Mixed Salts: Salt which are formed by the neutralisation reaction of more than two different acids and bases are called mixed salt. Or Salts which furnish more than one cation or more than one anion when dissolved in water are also as mixed salt. Like Rochelle Salt,

e.g., 

etc.

eg. $\boxed{\underset{\text{Two acids}}{Ca(OH)_2 + HOCl/HCl \rightarrow CaOCl_2}}$

Double Salts

Salts which are formed by the addition of two or more simple salts are called as double salt.

eg. $K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow$ Potash alum

eg. $FeSO_4.(NH_4)_2SO_4.6H_2O \rightarrow$ Mohr's salt etc.

SALT HYDROLYSIS (REVERSE OF NEUTRALISATION)

$$\text{Salt} + \text{Water} \rightleftharpoons \text{acid} + \text{base}$$

When acids and bases are mixed in equal amounts(equivalents), then we will be having salt solutions only in the water and we have to calculate pH of salt solutions.

When a salt is added to water, the solid salt first dissolves and breaks into ions completely(unless otherwise specified). The ions of the salt may or may not react with water, the cations when react with water will produce H_3O^+ ions and the anions on reaction with water will produce OH^- ions. Depending on the extent of hydrolysis and on the amounts of H_3O^+ and OH^- ions the solution can be acidic, basic or neutral. If salt is BA, then

$$BA(s) \rightarrow BA(aq) \rightarrow B^+(aq) + A^-(aq)$$

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

(anionic hydrolysis)

$$B^+(aq) + 2H_2O(l) \rightleftharpoons BOH(aq) + H_3O^+(aq)$$

(cationic hydrolysis)

ANIONIC HYDROLYSIS

Anions can function as a base on reaction with water and hydrolyse as follows:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

The extent of hydrolysis of a given anion depends on its basic strength

(*a*) **Complete hydrolysis:** The anions, which are stronger base than OH^- and the conjugate acids of the anions are weaker acid than H_2O, they will show complete hydrolysis in aqueous medium.

Example: $H^- + H_2O \rightarrow H_2 + OH^-$

$NH_2^- + H_2O \rightarrow NH_3 + OH^-$

(*b*) **Hydrolysis to a limited extent:** The anions, which are weaker base than OH^- and the conjugate acids are stronger acid than H_2O but weaker acid than H_3O^+ will hydrolyse to a limited extent in aqueous medium

Example: $CN^- + H_2O \rightleftharpoons HCN + OH^-$

Other Examples are CH_3COO^-, NO_2^-, S^{2-} etc.

(*c*) **No hydrolysis:** The anions that are weaker base than OH^- and the conjugate acids are stronger than both H_2O and H_3O^+ do not hydrolyse at all.

$Cl^- + H_2O \not\longrightarrow HCl + OH^-$

Other Examples include SO_4^{2-}, NO_3^-, ClO_4^- etc.

CATIONIC HYDROLYSIS

Cations can function as acid on reaction with water and hydrolysis as follows.

$$B^+(aq) + 2H_2O(l) \rightleftharpoons BOH(aq) + H_3O^+(aq)$$

The extent of hydrolysis of a given cation depends on its acidic strength.

(*a*) **Complete hydrolysis:** The cations, which are stronger acid than H_3O^+ and their conjugate bases are very much weaker than H_2O will show complete hydrolysis. Example is PH_4^+ ion.

$PH_4^+ + H_2O \rightarrow H_3O^+ + PH_3$

(*b*) **Hydrolysis to a limited extent:** The cations, which are weaker acid than H_3O^+ ion and their conjugate bases are stronger than H_2O but weaker than OH^-, show hydrolysis to a limited extent. For Example

$NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$

Other ions showing hydrolysis to limited extent are $C_6H_5NH_3^+$, $CH_3NH_3^+$ etc.

(*c*) **No hydrolysis:** The cations, which are weaker acid than H_3O^+ and their conjugate bases are stronger than both H_2O and OH^- do not hydrolyze at all. Example is alkali and alkaline earth metal ions.

$Na^+ + 2H_2O \not\longrightarrow NaOH + H_3O^+$

(A) Hydrolysis of strong acid and strong base [SA – SB] types of salt –

Ex. NaCl, $BaCl_2$, Na_2SO_4, $KClO_4$, $BaSO_4$, $NaNO_3$, KBr, KCl etc.

$NaCl + H_2O \rightleftharpoons NaOH + HCl$

$Na^+ + Cl^- + H_2O \rightleftharpoons Na^+ + OH^- + H^+ + Cl^-$

$H_2O(l) \rightleftharpoons H^+ + OH^-$ (It is not salt hydrolysis)

(*i*) Hydrolysis of salt of [SA – SB] is not possible.

(*ii*) Aqueous solution of these type of salt is neutral in nature. ($pH = pOH = 7$)

(*iii*) pH of the solution is 7.

(*iv*) No effect on litmus paper.

(B) Hydrolysis of strong acid and weak base [SA - WB] types of salt –

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$, AgCl, AgI, $AgNO_3$ etc

$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

[WB - SA]

$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

(*i*) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis.

(*ii*) Solution is acidic in nature as $[H^+]$ is increased.

(*iii*) pH of the solution is less than 7.

(*iv*) Solution turns blue litmus paper red.

Credit:--- Divansh.....

K_h = Hydrolysis constant
K_W = Ionic product of water
K_a = Ionisation constant of acid
K_b = Ionisation constant of base
h = Degree of hydrolysis
C = Concentration of salt (concentration of ions)

(a) Relation between K_h, K_W and K_b

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad ...(1)$$

For weak Base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} \qquad ...(2)$$

For water $H_2O \longrightarrow H^+ + OH^-$

$$K_W = [H^+]\,[OH^-] \qquad ...(3)$$

Now multiplying Eq. (1) and (2) = Eq. (3)

$$\frac{\left[NH_4OH\right]\left[H^+\right]}{\left[NH_4^+\right]} \times \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} = [H^+]\,[OH^-]$$

i.e. $K_h \times K_b = K_W$

$$\boxed{K_h = \frac{K_W}{K_b}} \qquad ...(4)$$

(b) Degree of hydrolysis – (h)

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Initial concentration of salt

$$\begin{array}{ccc} C & 0 & 0 \\ C-Ch & Ch & Ch \end{array}$$

$$K_h = \frac{[NH_4OH]\left[H^+\right]}{\left[NH_4^+\right]} = \frac{Ch \times Ch}{C - Ch}$$

$$= \frac{C^2h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since h <<<< 1 then (1 – h) ≈ 1

$$\therefore \boxed{K_h = Ch^2} \qquad ...(5)$$

$$h^2 = \frac{K_h}{C} \Rightarrow h = \sqrt{\frac{K_h}{C}} \qquad ...(6)$$

$$\therefore K_h = \frac{K_W}{K_b} \Rightarrow h = \sqrt{\frac{\frac{K_W}{K_b}}{C}}$$

$$h = \sqrt{\frac{K_W}{K_b \times C}} \qquad ...(7)$$

(c) pH of the solution: pH = – log [H^+]

$$[H^+] = Ch = C\sqrt{\frac{K_W}{K_b \times C}} \Rightarrow [H^+] = \sqrt{\frac{K_W \times C}{K_b}} \qquad ...(8)$$

taking – log on both sides

$$-\log [H^+] = -\log \sqrt{\frac{K_W \times C}{K_b}}$$

$$\Rightarrow pH = -\log \left(\frac{K_W \times C}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}\,[\log K_W + \log C - \log K_b]$$

$$pH = -\frac{1}{2}\log K_W - \frac{1}{2}\log C - \frac{1}{2}(-\log K_b)$$

$$pH = \frac{1}{2}pK_W - \frac{1}{2}\log C - \frac{1}{2}pK_b$$

$$\boxed{pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C} \qquad ...(9)$$

(C) Hydrolysis of weak acid and strong base [WA – SB] types of salt –

Ex. CH_3COONa, $HCOONa$, KCN, $NaCN$, K_2CO_3, $BaCO_3$, K_3PO_4 etc.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

- In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis.
- Solution is basic in nature as [OH^-] increases.
- pH of the solution is greater than 7.
- Solution turns red litmus paper blue.

(i) Relation between K_h, K_W and K_a

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$K_h = \frac{[CH_3COOH]\left[OH^-\right]}{\left[CH_3COO^-\right]} \qquad ...(1)$$

For weak acid $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{[CH_3COOH]} \qquad ...(2)$$

For water $H_2O \longrightarrow H^+ + OH^-$

$$K_W = [H^+]\,[OH^-] \qquad ...(3)$$

Now multiply eq. (1) × eq. (2) = eq. (3)

$$\frac{[CH_3COOH]\left[OH^-\right]}{\left[CH_3COO^-\right]} \times \frac{\left[CH_3COO^-\right]\left[H^+\right]}{[CH_3COOH]}$$

$= [H^+][OH^-]$

$K_h \times K_a = K_W$

$$\boxed{K_h = \frac{K_W}{K_a}} \qquad ...(4)$$

Credit:--- Divansh.....

(ii) Degree of hydrolysis (h):

$$
\begin{array}{lccc}
CH_3COO^- + H_2O & \rightleftharpoons & CH_3COOH + & OH^- \\
C & & 0 & 0 \\
C - Ch & & Ch & Ch
\end{array}
$$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)}$$

$$K_h = \frac{Ch^2}{(1-h)}$$

Since $h <<<< 1$ then $(1-h) \approx 1$

$$\therefore \boxed{K_h = Ch^2} \qquad ...(5)$$

$$h^2 = \frac{K_h}{C} \text{ or } h = \sqrt{\frac{K_h}{C}} \qquad ..(6)$$

$$\boxed{h = \sqrt{\frac{K_W}{K_a \times C}}} \qquad ...(7)$$

(iii) pH of the solution

$[OH^-] = Ch$

$$[OH^-] = C \times \sqrt{\frac{K_W}{K_a \times C}} \text{ or } [OH^-] = \sqrt{\frac{K_W \times C}{K_a}}$$

$\therefore K_W = [OH^-][H^+]$

$$\therefore [H^+] = \frac{K_W}{[OH^-]} = \frac{K_W}{\sqrt{\frac{K_W \times C}{K_a}}}$$

$$\boxed{[H^+] = \sqrt{\frac{K_W \times K_a}{C}}} \qquad ...(8)$$

taking – log on both sides

$$-\log [H^+] = -\log \sqrt{\frac{K_W \times K_a}{C}}$$

$$pH = -\log \left(\frac{K_W \times K_a}{C}\right)^{1/2}$$

$$pH = -\frac{1}{2}[\log K_W + \log K_a - \log C]$$

$$pH = -\frac{1}{2}\log K_W - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

$$pH = \frac{1}{2}pK_W + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C \qquad ...(9)$$

(D) Hydrolysis of weak acid and weak base (WA - WB) type of salt:

Ex. CH_3COONH_4, AgCN, NH_4CN, $CaCO_3$, $[NH_4]_2CO_3$, $ZnHPO_3$ etc.

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

- ✦ Solution is almost neutral but it may be acidic or basic depending upon the nature of acid and base.

(a) Relation between K_h, K_w, K_a and K_b

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \qquad ...(1)$$

For weak base $NH_4OH \longrightarrow NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad ...(2)$$

For weak acid $CH_3COOH \longrightarrow CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ...(3)$$

For water

$H_2O \longrightarrow H^+ + OH^-$

$$K_W = [H^+][OH^-] \qquad ...(4)$$

Multiply Eq. (1) × Eq. (2) × Eq. (3) = Eq. (4)

$$\frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} \times \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = [H^+][OH^-]$$

$$K_h \times K_b \times K_a = K_W$$

$$\boxed{K_h = \frac{K_W}{K_a \times K_b}} \qquad ...(5)$$

(b) Degree of hydrolysis (h) –

$$
\begin{array}{lcccc}
CH_3COO^- + & NH_4^+ + H_2O & \rightleftharpoons & CH_3COOH + & NH_4OH \\
C & C & & 0 & 0 \\
C - Ch & C - Ch & & Ch & Ch
\end{array}
$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{Ch \times Ch}{(C - Ch)(C - Ch)}$$

$$= \frac{C^2h^2}{C(1-h) \times C(1-h)}$$

Since $h <<<< 1$ then $(1-h) \approx 1$

$$\therefore \boxed{K_h = h^2} \qquad ...(6)$$

$$\text{or } h^2 = \frac{K_W}{K_a \times K_b} \text{ or } \boxed{h = \sqrt{\frac{K_W}{K_a \times K_b}}} \qquad ...(7)$$

(c) pH of the solution

from equation (3)

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1-h}$$

Since $h <<<< 1$ then $(1-h) \approx 1$

Credit:--- Divansh.....

$[H^+] = K_a \times h$ [Now put the value of h from eq. (7)]

$$= K_a \times \sqrt{\frac{K_W}{K_a \times K_b}}$$

$$\boxed{[H^+] = \sqrt{\frac{K_W \times K_a}{K_b}}} \quad ...(8)$$

taking −log on both sides −log [H⁺]

$$= -\log\left(\frac{K_W \times K_a}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}[\log(K_w \times K_a) - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_W + \log K_a - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_W] - [\log K_a] - [-\log K_b]$$

$$pH = +\frac{1}{2}pK_W + pK_a - \frac{1}{2}pK_b$$

$$\boxed{pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b} \quad ...(9)$$

Note: Degree of hydrolysis of weak acid and weak base [WA–WB] type salt does not depend on the concentration of salt.

For WA - WB types of salt:

	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic anionic	Anionic cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	pH < 7	pH > 7	pH = 7

SUMMARY

Types of Salts	K_h	h	pH
SASB	–	–	7
WASB	K_w/K_a	$\sqrt{\frac{K_w}{K_a \times C}}$	$7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$
SAWB	K_w/K_b	$\sqrt{\frac{K_w}{K_b \times C}}$	$7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$
WAWB	$\frac{K_W}{K_a \times K_b}$	$\sqrt{\frac{K_W}{K_a \times K_b}}$	$7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

Hydrolysis of amphiprotic anion (Cation is not hydrolysed)

Some salts like NaHS, $NaHCO_3$, Na_2HPO_4 etc can undergo both ionization and hydrolysis.

Example.

$$HCO_3^- + H_2O \xrightleftharpoons{\text{Ionisation}} CO_3^{2-} + H_3O^+$$

$$HCO_3^- + H_2O \xrightleftharpoons{\text{Hydrolysis}} H_2CO_3 + OH^-$$

Thus, HCO_3^- is amphiprotic anion

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-, K_{a_1}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^-, K_{a_2}$$

$$pH = \frac{pKa_1 + pKa_2}{2}$$

Similarly, $H_2PO_4^-$ and HPO_4^{2-} are amphiprotic anions.

$$pH(H_2PO_4^-) = \frac{pKa_1 + pKa_2}{2}$$

$$pH(HPO_4^{2-}) = \frac{pKa_2 + pKa_3}{2}$$

Since $H_2PO_4^-$ is involved between HPO_4^{2-} and H_3PO_2. Hence, we can use pK_{a_1} and pK_{a_2} values in hydrolysis of $H_2PO_4^-$. In HPO_4^{2-}. We can use pK_{a_2} and pK_{a_3} value since it is involved between PO_4^{3-} and HPO_4^{2-}.

Train Your Brain

Example 30: What is the percentage hydrolysis of a 0.003 M aqueous solution of NaOCN? where K_a for HOCN = 3.33×10^{-4}.

(*a*) 10^{-2} (*b*) 10^{-3} (*c*) 10^{-4} (*d*) 10^{-5}

Sol. $OCN^- + H_2O \longrightarrow HOCN + OH^-$

$$h^2 = \frac{K_w}{CK_a} = 10^{-8}$$

$$h = 10^{-4}$$

So, % hydrolysis = 10^{-2}%

Example 31: The pH of 0.02 M NH_4Cl(aq.) (pK_b = 4.73) is equal to:

(*a*) 3.78 (*b*) 4.73 (*c*) 5.48 (*d*) 7.00

Sol. $pH = \frac{1}{2}[pK_w - pK_b - \log C]$

$$= \frac{1}{2}[14 - 4.73 - \log 0.02]$$

$$= \frac{1}{2}[14 - 4.73 + 1.698] = 5.48$$

Example 32: pH of 0.05 M $(CH_3COO)_2Ca$ (pK_a = 4.74) is

(*a*) 8.72 (*b*) 8.87 (*c*) 7 (*d*) 1.30

Sol. $[CH_3COO^-] = 2 \times 0.05 = 0.1$

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + 4.74 + \log 0.1]$$

$$= \frac{1}{2}[14 + 4.74 - 1] = 8.87$$

Credit:--- Divansh.....

Concept Application

39. The salt of which of the following four weak acids will be most hydrolysed:
(a) HA ; $K_a = 1 \times 10^{-8}$ (b) HB ; $K_a = 2 \times 10^{-6}$
(c) HC ; $K_a = 3 \times 10^{-8}$ (d) HD ; $K_a = 4 \times 10^{-10}$

40. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be
(a) 4.79 (b) 7.01 (c) 9.22 (d) 9.58

41. A salt of strong acid and weak base is dissolved in water. Its hydrolysis in solution is-
(a) unaffected on heating
(b) increased by adding strong acid
(c) suppressed by diluting
(d) suppressed by adding strong acid

42. The dissociation constant of CH_3COOH is 1.8×10^{-5}. The hydrolysis constant for 0.1 M sodium acetate is -
(a) 5.56×10^{4} (b) 5.56×10^{-10}
(c) 1.8×10^{-5} (d) 1.8×10^{9}

43. The degree of hydrolysis of which of the following salt is independent of the concentration of salt solution ?
(a) CH_3COONa (b) NH_4Cl
(c) CH_3COONH_4 (d) NaCl

BUFFER SOLUTIONS

Buffer Solutions are those, which resist to change in pH upon addition of small amount of acid or base. this does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

(i) In certain applications of chemistry and biochemistry we require solutions of constant pH. Such solution are called buffer solution.

(ii) A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called buffer solution.

(iii) Buffer solutions are also called solutions of reverse acidity or alkalinity.

(iv) Following are the characteristics of buffer solutions
- (a) It must have almost constant pH.
- (b) Its pH should not be changed on long standing
- (c) Its pH should not be changed on dilution.
- (d) It pH should not be changed to any great extent on addition of small quantity of acid or base.

(v) Buffer solutions can be classified as follows.
- (a) Simple buffer
- (b) Mixed buffer

SIMPLE BUFFER

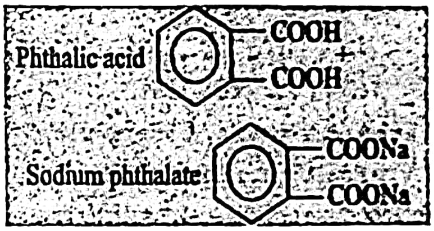
It is a solution of one compound i.e. salts of WA + WB

Simple buffer solutions have very little significance since $pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$ so solution of desired pH can not be prepared.

Mixed buffer: Mixed buffers are solutions of more than one compounds They can be further classified as
- (a) Acidic buffer
- (b) Basic buffer

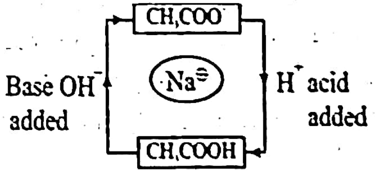
ACIDIC BUFFER

(i) These are the mixture of a weak acid and its salt with strong base.
e.g.
(a) $CH_3COOH + CH_3COONa$
(b) Boric acid (H_3BO_3) + Borax ($Na_2B_4O_7$)
(c)



(ii) Buffer action of acidic buffer can be explained with following equilibria,
(a) $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
(Feebly ionised.)
(b) $CH_3COONa \rightarrow Na^+ + CH_3COO^-$
(completely ionised.)
(c) $H_2O \rightleftharpoons H^+ + OH^-$
When a strong acid is added in the solution $[H^+]$ increases, which will combine with CH_3COO^- to form feebly ionised CH_3COOH, which is also suppressed by common ion effect,
$CH_3COO^- + H^+ \text{ (from acid)} \rightleftharpoons CH_3COOH$
(weak Acid)
Again when strong base is added in the solution it will attack on unionised acid CH_3COOH to form feebly ionised H_2O molecules
$CH_3COOH + OH^- \text{ (from base)} \rightleftharpoons CH_3COO^- + H_2O$

(iii) One can remember the buffer action of acidic buffer with the help of following figure -



(iv) pH of such acidic buffer can be calculated as follows.
(a) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+ (K_a)$
(b) $CH_3COONa \xrightarrow{H_2O} CH_3COO^-(aq.) + Na^+(aq.)$

Credit:--- Divansh.....

CH_3COOH is feebly ionised and its ionisation is also suppressed by presence of common ion (CH_3COO^-). So one can fairly assume $[CH_3COO^-] = [salt]$ and $[CH_3COOH] = [Acid]$ taken initially in buffer solution.

$$\text{so } K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\text{or } [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$\text{or} \quad pH = pk_a + \log\frac{[Salt]}{[Acid]}$$

Above equation is called Henderson's equation.

- If we increase the concentration of given salt in acidic buffer, pH will also increase.
- If we increase the concentration of acid in acidic buffer, pH will decreases.
- If conc. and volume are given for salt and acid then the pH is given by the following formula-

$$pH = pK_a + \log\frac{[N_2V_2]}{[N_1V_1]}$$

Where N_2V_2 = normality & volume of salt

N_1V_1 = normality & volume of acid

Note: Mixture of weak acid and strong base solution can also act as an acidic buffer, if no. of eqv. of weak acid is greater than the no. of eqv. of strong base.

BASIC BUFFER

(*i*) These are the mixture of a weak base and its salt with strong acid.

e.g.

(*a*) $NH_4OH + NH_4Cl$

(*b*) Glycine (NH_2CH_2COOH) + Glycine hydrochloride ($Cl^- + N^+H_3CH_2COOH$)

(*ii*) Buffer action of basic buffer can be explained with the help of following equilibria

(*a*) $NH_4OH \rightleftharpoons NH_4^+ + OH^- (K_b)$

(*b*) $NH_4Cl \rightarrow NH_4^+ + Cl^-$

(*c*) $H_2O \rightleftharpoons H^+ + OH^- (K_w)$

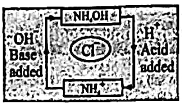
When a strong base is added in the solution $[OH^-]$ increases, which will combine with NH_4^+ to form feebly ionised NH_4OH, which is also suppressed by common ion effect.

$NH_4^+ + OH^-$ (From base) $\rightleftharpoons NH_4OH$ (Weak base)

Again when strong acid is added in the solution it will attack on unionised base NH_4OH to form feebly ionised H_2O molecules.

$NH_4OH + H^+$ (From acid) $\rightarrow NH_4^+ + H_2O$

(*iii*) One can remember the buffer action of basic buffer with the help of following figure -



(*iv*) pH of such basic buffer can be calculated from Henderson-Hasselbalch equation as follows.

(*a*) $NH_4OH \rightleftharpoons NH_4^+ + OH^-(K_b)$

(*b*) $NH_4Cl \rightarrow NH_4^+ (aq.) + Cl^-(aq.)$

NH_4OH is feebly ionised and its ionisation is also surpressed by presence of common ion (NH_4^+). So one can fairly assume $[NH_4^+] = [Salt]$ and $[NH_4OH] = [Base]$ taken initially in buffer solution.

$$\text{so} \quad K_b = \frac{[OH^-][NH_4^+]}{[NH_4OH]}$$

$$\text{or} \quad [OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]} = \frac{K_b[Base]}{[Salt]}$$

$$\text{or} \quad pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

This is known as the Henderson's equation of a buffer. or $pH = 14 - pOH$

BUFFER CAPACITY

(*i*) The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.

(*ii*) Buffer capacity is number of moles of acid or base added in one litre of solution as to change the pH by unity, i.e.

$$\text{Buffer capacity} = \frac{\text{Number of moles acid or base added to 1 lit. sol.}}{\text{Change in pH}}$$

Maximum buffer capacity: It can be proved that the maximum buffer is achieved when the salt and acid or base concentration is equal.

Train Your Brain

Example 33: The pH of a blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$. What volume of 5M $NaHCO_3$ solution should be mixed with 10 ml of a sample of solution which is 2.5 M in H_2CO_3 (assume no $NaHCO_3$), in order to maintain a pH = 7.4.(pK_a for H_2CO_3 = 6.7, log 2 = 0.3)

Sol. $pH = pK_a + \log\frac{[salt]}{[base]}$

$\Rightarrow 7.4 = 6.7 + \log\frac{[salt]}{[base]} \Rightarrow \frac{[salt]}{[base]} = 5$

$\Rightarrow 5 \times 2.5 \times 10 \times 10^{-3} = 5 \times V$

$\Rightarrow$ required volume = 25 ml

Example 34: 20 mL of 0.2 M NaOH are added to 50 mL of 0.2 M acetic acid ($Ka = 1.8 \times 10^{-5}$).

(*a*) What is pH of solution?

(*b*) Calculate volume of 0.2 M NaOH required to make the pH of solution 4.74.

Sol. (*a*) $NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$

	NaOH	CH_3COOH	CH_3COONa	H_2O
Millimole added	20×0.2	50×0.2	0	0
Millimole	= 4	= 10	0	0
after reaction	0	6	4	4

$\therefore \quad [Molarity] = \frac{\text{millimole}}{\text{Total volume}}$

$\therefore \quad [CH_3COOH] = \frac{6}{70}; [CH_3COONa] = \frac{4}{70}$

$\therefore \quad pH = -\log(1.8 \times 10^{-5}) + \log\frac{4/70}{6/70} = 4.56$

(*b*) Let V mL of 0.2 M NaOH is required to make pH 4.74 then

$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$

	NaOH	CH_3COOH	CH_3COONa	H_2O
Millimole added	0.2×V	50 × 0.2	0	0
Millimole after reaction	0	(10 – 0.2 V)	0.2 V	0.2V

$\therefore [Acid] = \frac{10-0.2V}{50+V};$

$[Salt] = \frac{0.2V}{50+V}$

$\therefore 4.74 = -\log(1.8 \times 10^{-5}) + \log\frac{(0.2V)/(50+V)}{(10-0.2V)/(50+V)}$

$\therefore \quad V = 25$ mL

Example 35: Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH = 9, when total concentration of buffering reagents is 0.6 mol litre^{-1}. pK_b for NH_3 = 4.7, log 2 = 0.30

Sol. $pOH = -\log K_b + \log\frac{[Salt]}{[Base]}$

$5 = 4.7 + \log\frac{a}{b}$

$\frac{a}{b} = 2$

$\therefore \quad a = 2b.$

Given $\quad a + b = 0.6$

$2b + b = 0.6$

$\therefore \quad 3b = 0.6$

or $\quad b = 0.2$ mole and $a = 0.4$ mole

Thus, [Salt] = 0.4 M and [Base] = 0.2 M

Credit:--- Divansh.....

Concept Application

44. What is $[H^+]$ of a solution that is 0.1M HCN and 0.2 M NaCN ? (K_a for HCN = 6.2×10^{-10})
(a) 3.1×10^{10}
(b) 6.2×10^{5}
(c) 6.2×10^{-10}
(d) 3.1×10^{-10}

45. The pH of a buffer is 4.745. When 0.01 mole of NaOH is added to 1 litre of it, the pH changes to 4.832. Calculate its buffer capacity
(a) 0.01 (b) 0.115 (c) 0.126 (d) 0.02

46. A solution is prepared by mixing equal volumes of 0.4 M CH_3COOH and 0.2 M CH_3COONa. K_a for $CH_3COOH = 10^{-6}$. The pH of the resulting solution would be -
(a) 6 (b) 5.69 (c) 6.69 (d) 6.5

47. A buffer solution contains 1 mole of $(NH_4)_2SO_4$ and 1 Mole of NH_4OH ($K_b = 10^{-5}$). The pH of solution will be:
(a) 5
(b) 9
(c) 5.3010
(d) 8.6990

INDICATOR

Introduction

- **Definition:** Those compound or substance which indicate the nature of solution by changing their self colour.
- **Types of indicators:**
  (a) **Acidic indicator (HIn)**
  Ex. Phenolphthalein (HPh)
  $HPh \rightleftharpoons H^+ + Ph^-$
  colourless — pink
  (b) **Basic indicator (InOH)**
  Ex. Methyl orange (MeOH)
  $MeOH \rightleftharpoons Me^+ + OH^-$
  yellow — orange red

OSTWALD THEORY OF INDICATORS

(i) According to this theory, all the indicators are weak organic acid or base.

(ii) Every indicator has light colour in its unionised form and dark colour in ionised form.

(iii) Every indicator works in opposite medium (it means if it is acidic then it will work in basic medium and vice versa) it means colour change in opposite medium as their unionised form is changed into ionised form.

Ex. Acidic indicator [HPh]

Case 1: $HPh \rightleftharpoons H^+ + Ph^-$
In acidic medium $[H^+]$ — $[HPh] > [Ph^-]$
Colourless

Case 2: $HPh \rightleftharpoons H^+ + Ph^-$
In basic medium $[OH^-]$ — $[Ph^-] > [HPh]$
Pink colour

(a) pH of acidic indicator -

$$HIn \rightleftharpoons H^+ + In^-$$

$$K_I = \frac{[H^+][In^-]}{[HIn]}$$

$$[H^+] = \frac{K_I[HIn]}{[In^-]}$$

Taking – log on both sides

$$pH = pK_I - \log[HIn] + \log[In^-]$$

$$pH = pK_I + \log\frac{[In^-]}{[HIn]}$$

$$\boxed{pH = pK_I + \log\frac{[\text{Ionised form}]}{[\text{Unionised form}]}}$$

(b) pOH of basic indicator -

$$InOH \rightleftharpoons In^+ + OH^-$$

$$K_I = \frac{[In^+][OH^-]}{[InOH]}$$

$$\boxed{pOH = pK_I + \log\frac{[\text{Ionised form}]}{[\text{Unionised form}]}}$$

(c) pH range of acidic indicator:

[HIn]	:	$[In^-]$
1	:	10
10	:	1

$$\boxed{pH = pK_I \pm 1}$$

(d) pOH range of basic indicator:

[InOH]	:	$[In^+]$
1	:	10
10	:	1

$$\boxed{pOH = pK_I \pm 1}$$

(e) Neutral condition for indicators (No working condition)

For acidic indicator	For basic indicators
$[HIn] : [In^-]$	$[InOH] : [In^+]$
1 : 1	1 : 1
$\boxed{pH = pK_I}$	$\boxed{pOH = pK_I}$

Selection of Indicator

Near the equivalence point of acid base titration, the pH value of the solution changes steeply and the pH range of this steep change depends on the nature of the acid-base pair being titrated. For titration involving weak acid or weak base, the salt formed undergoes hydrolysis and therefore, pH value is either greater than 7 or less than 7. The selected indicator should be such that it offers a colour change near the vicinity of the pH of the solution at the equivalence point.

Thus, selection of indicator must satisfy the following points;

1. The steep selection of the titration curve at the equivalence point must encompass an interval of pH values at least as large as the pH transition range of the indicator.
2. The pH transition range of the indicator coincide with steep portion of the titration curve

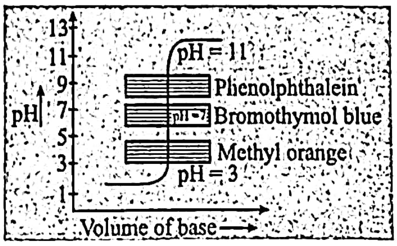
Indicator	Acid form	Base-form	Acid form at pH	Base form at pH
Phenolphthalein	Colourless	Pink	8.3	10.0
Methyl orange	Red	Yellow	3.1	4.4
Methyl Red	Red	Yellow	4.2	6.2
Phenol Red	Yellow	Red	6.2	8.2
Litmus	Red	Blue	4.5	8.3
Malachite green	Yellow	Green	0.0	2.0
AJizann blues	Green	Blue	11.0	13.0

Key Note

- ❖ Phenolphthalein cannot be used as indicator in the titration of strong acid and weak base

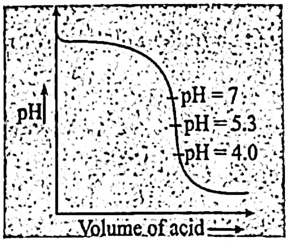
Plots of pH values by using different indicators

(i) Titration of strong acid by strong base, Both acidic as well as basic indicators are suitable



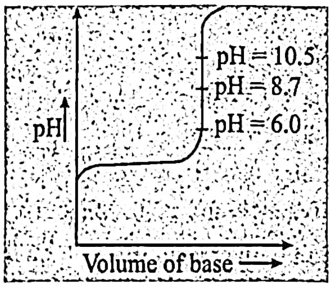
Example: Methyl orange and phenolphthalein

(ii) Titration of weak base by a strong acid, Only acidic indicators are suitable



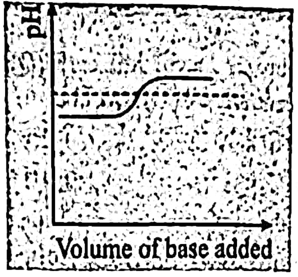
Example: Methyl orange

(iii) Titration of weak acid by strong base, Only basic indicators are suitable.



Example: Phenolphthalein

(*iv*) Titration of weak acid with weak base, No indicator is suitable as such



ACID-BASE TITRATION

S.No.	Type of titration	pH range of titration	Suitable indicators
1.	SA/SB	3 – 11	All indicators (MeOH, HPh etc.)
2.	SA/WB	3 – 7	Methyl orange (MeOH) and methyl red
3.	WA/SB	7 – 11	Phenolphthalein (HPh)
4.	WA/WB	6.5 – 7.5	Phenol red

Train Your Brain

Example 36: Indicator used in the titration of sodium carbonate and hydrochloric acid is –

(*a*) phenolphthalein (*b*) diphenyl amine

(*c*) starch (*d*) methyl orange

Sol. Methyl orange indicator (pH range 3.0 – 4.4) is used for titration of a strong acid with a strong or weak base.

Concept Application

48. The pink colour of phenolphthalein in alkaline medium is due to

(*a*) the acidic form of phenolphthalein

(*b*) the anionic form of phenolphthalein

(*c*) OH^- of the alkali

(*d*) The non conjugated structure of phenolphthalein

49. A certain monoprotic acid (weak) serves as indicator. Assuming that colour change is seen when 1/3rd of the indicator has been converted to ions and that at end point the pH of solution is 6, what is the value of pK_{in}?

(*a*) 7.306 (*b*) 6.307 (*c*) 4.302 (*d*) 3.302

SOLUBILITY AND SOLUBILITY PRODUCT (K_{SP})

Solubility

(*a*) **Definition:**

At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called solubility.

(*b*) **Important points:** Solubility does not depend on amount of substances and volume of solution where as it depends on the following –

(*i*) Temperature

(*ii*) Presence of common ion

(*iii*) Nature of solvent

SOLUBILITY PRODUCT (K_{SP})

(*a*) At constant temperature in equilibrium state, the product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which further dissolution of even a small amount of salt is not possible).

Ex. (*i*) Let solubility of AgCl is S mol L^{-1}

$$\begin{array}{lcccccc} & AgCl & \rightleftharpoons & Ag^+ & + & Cl^- \\ & a & & 0 & & 0 \\ \text{After saturation} & a-S & & S & & S \end{array}$$

According to L.M.A.

Solubility product at saturation in terms of concentration of ions $K_{sp} = [Ag^+][Cl^-]$

Solubility product in terms of solubility $K_{sp} = (S)(S)$

$$\boxed{K_{sp} = S^2}$$

$$\begin{array}{lccc} \textbf{Ex. } (ii)\ K_{sp} \text{ for } CaCl_2 & CaCl_2 \rightleftharpoons & Ca^{+2} + & 2Cl^- \\ \text{Initially} & a & 0 & 0 \\ \text{Let solubility of } CaCl_2 & a-S & S & 2S \\ \text{is S mol L}^{-1} & & & \end{array}$$

Solubility product in terms of concentration of ions

$K_{sp} = [Ca^{+2}][Cl^-]^2$

In terms of solubility $K_{sp} = (S)(2S)^2$

$$\boxed{K_{sp} = S^3}$$

$$\begin{array}{lccc} \textbf{Ex. } (iii)\ K_{sp} \text{ for } AlCl_3 & AlCl_3 \rightleftharpoons & Al^{+3} + & 3Cl^- \\ \text{Initially} & a & 0 & 0 \\ \text{Let solubility of } AlCl_3 & a-S & S & 3S \\ \text{is S mol L}^{-1} & & & \end{array}$$

Solubility product in terms of concentration of ions

$K_{sp} = [Al^{+3}][Cl^-]^3$

In terms of solubility $K_{sp} = (S)(3S)^3$

$$\boxed{K_{sp} = 27S^4}$$

(*b*) General form

$$\begin{array}{lccc} & A_xB_y \rightleftharpoons & xA^{y+} & +yB^{x-} \\ & a & 0 & 0 \\ & a-S & xS & yS \end{array}$$

$K_{sp} = [A^{y+}]^x [B^{x-}]^y$

$= [xs]^x \times [ys]^y = x^x.s^x.y^y.s^y$

$$\boxed{K_{sp} = x^x y^y S^{(x+y)}}$$

Ex.

(*i*) $Al_2(SO_4)_3$

$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108\ S^5$

(*ii*) Na_2KPO_4

$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$

(*iii*) $NaKRbPO_4$

$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$

Train Your Brain

Example 37: Solubility product constants (K_{sp}) of salts of types MX, MX_2, M_3X at temperature T are 4×10^{-8}, 3.2×10^{-14} and 2.7 A× 10^{-15} respectively. Solubility (mol dm^{-3}) of the salts at temperature T are in the order -

(*a*) $MX > MX_2 > M_3X$ (*b*) $M_3X > MX_2 > MX$

(*c*) $MX_2 > M_3X > MX$ (*d*) $MX > M_3X > MX_2$

Sol. (*d*) Solubility (S_1) of

$$MX = \sqrt{K_{sp}} = \sqrt{4\times10^{-8}} = 2\times10^{-4}M$$

Solubility (S_2) of

$$MX_2 = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2\times10^{-14}}{4}\right)^{1/3} = 2\times10^{-5}M$$

Solubility (S_3) of

$$M_3X = \left(\frac{K_{sp}}{27}\right)^{1/4} = \left(\frac{2.7\times10^{-15}}{27}\right)^{1/4} = 10^{-4}M$$

$\therefore S_1 > S_3 > S_2$

Example 38: The solubility product K_{sp} of the sparingly soluble salt Ag_2CrO_4 is 4×10^{-12}. The solubility of the salt is-

(*a*) 1×10^{-12} mol L^{-1} (*b*) 2×10^{-6} mol L^{-1}

(*c*) 1×10^{-6} mol L^{-1} (*d*) 1×10^{-4} mol L^{-1}

Sol. (*d*) $K_{sp} = 4s^3 = 4 \times 10^{-12} = 4s^3$

$s = 10^{-4}$

Example 39: Compound AB gets 80% ionised. What should be the solubility of AB, if its solubility product is 6.4×10^{-9}?

Sol.

$$\begin{array}{lcc} AB \rightleftharpoons & A^+ & B^- \\ s & 0.8s & 0.8s \end{array}$$

$K_{sp} = [A^+][B^-]$

$6.4 \times 10^{-9} = 0.8s \times 0.8s$

$$0.64\ s^2 = 6.4 \times 10^{-9} \text{ or } s^2 = \frac{6.4\times10^{-9}}{0.64} = 10^{-8}$$

$\therefore s = 10^{-4}$ mol/L

Concept Application

50. If solubility product of the base $M(OH)_3$ is 2.7×10^{-11}, the concentration of OH^- will be

(*a*) 3×10^{-3} (*b*) 3×10^{-4}

(*c*) 10^{-3} (*d*) 10^{-11}

51. What is the minimum concentration of SO_4^{2-} required to precipitate $BaSO_4$ in a solution containing 1.0×10^{-4} mole/L of Ba^{2+}?

K_{sp} for $BaSO_4 = 4 \times 10^{-10}$:

(*a*) 4×10^{-10} M (*b*) 2×10^{-7} M

(*c*) 4×10^{-6} M (*d*) 2×10^{-3} M

52. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product will be -

(*a*) 1×10^{-15} (*b*) 1×10^{-10}

(*c*) 4×10^{-15} (*d*) 4×10^{-10}

53. If x mol L^{-1} is the solubility of $KAl(SO_4)_2$, then K_{sp} is equal to:

(*a*) x^3 (*b*) $4x^4$

(*c*) x^4 (*d*) $4x^3$

APPLICATION OF SOLUBILITY PRODUCT (K_{SP})

- **To find out the solubility (S):**

(*i*) **K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt–**

Ex. NaCl, $BaSO_4$, CH_3COONa, $CaCO_3$, NaCN, KCN, NH_4CN, NH_4Cl etc.

$$\begin{array}{lcc} AB(s) \rightleftharpoons & A^+ + & B^- \\ 1 & 0 & 0 \\ 1-s & s & s \end{array}$$

$K_{sp} = [A^+] [B^-]$

$K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

(*ii*) **K_{sp} of AB_2 or A_2B (Mono-di or di-mono valency) type salt –**

Ex. $CaCl_2$, $CaBr_2$, K_2S, $(NH_4)_2SO_4$, K_2SO_4, K_2CO_3 etc.

$$\begin{array}{lcc} AB_2(s) \rightleftharpoons & A^{+2} + & 2B^- \\ 1 & 0 & 0 \\ 1-s & s & 2s \end{array}$$

$K_{sp} = [A^{+2}] [B^-]^2$

$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$

$$s = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

(*iii*) **K_{sp} of AB_3 or A_3B (Mono-tri or tri-mono valen type salt–**

Ex. $FeCl_3$, $AlCl_3$; K_3PO_4 etc.

$$\begin{array}{lcc} AB_3(s) \rightleftharpoons & A^{+3} + & 3B^- \\ 1 & 0 & 0 \\ 1-s & s & 3s \end{array}$$

$$K_{sp} = \left[A^{+3}\right]\left[B^-\right]^3 = s\times(3s)^3 = 27s^4 = 27s^4$$

$$s = \left(\frac{K_{sp}}{27}\right)^{1/4}$$

(*iv*) **K_{sp} of A_2B_3 or A_3B_2 (Di-tri or tri-di valency) type salt**

Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.

$$\begin{array}{lcc} A_2B_3(s) \rightleftharpoons & 2A^{+3} + & 3B^{-2} \\ 1 & 0 & 0 \\ 1-s & 2s & 3s \end{array}$$

$$K_{sp} = \left[A^{+3}\right]^2\left[B^{-2}\right]^3 = 2s\times2s\times3s\times3s\times3s = 108s^5$$

$$s = \left(\frac{K_{sp}}{108}\right)^{1/5}$$

- **Common ion effect on solubility:**

Important point: Solubility of substance always decreases in the presence of common ion.

Illustration 1

(*i*) Find out the solubility of AgCl in the presence of C NaCl solution?

$$\begin{array}{lcc} AgCl \rightleftharpoons & Ag^+ + & Cl^- \\ S & S & S \end{array}$$

In NaCl solution

$$\begin{array}{lccc} NaCl & \rightleftharpoons & Na^+ & + Cl^- \\ C & & C & C+S' \end{array}$$

Let solubility of AgCl in the presence of NaCl solution is S' mol L^{-1}.

$$\begin{array}{lcccc} AgCl & \rightleftharpoons & Ag^+ & + & Cl^- \\ S' & & S' & & S'+C \end{array}$$

According to L.M.A.

$K_{sp} = [Ag^+]' [Cl^-]'$

$K_{sp} = S' \ (S'+C) = S'^2 + S'C$

(Neglecting the higher power terms of S')

$K_{sp} = S'C$

$$\boxed{S' = \frac{K_{sp}}{C}}$$

Illustration 2

(*ii*) Find out the solubility of $CaCl_2$ solution in the presence of C NaCl solution?

$$\begin{array}{lcccc} CaCl_2 & \rightleftharpoons & Ca^{+2} & + & 2Cl^- \\ S & & S & & 2S \end{array}$$

For NaCl solution

$NaCl \rightleftharpoons Na^+ + Cl^-$

C C C

Let solubility of $CaCl_2$ in the presence of NaCl solution is S' mol L^{-1}.

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

S' S' 2S' + C

According to L.M.A.

$K_{sp} = [Ca^{+2}]'[Cl^-]'^2$

$K_{sp} = S'(2S' + C)^2 = S'(4S'^2 + 4S'C + C^2)$

$K_{sp} = 4S'^3 + 4S'^2C + S'C^2$

(Neglecting the higher power terms of S')

$$\boxed{S' = \frac{K_{sp}}{C^2}}$$

Illustration 3

(*iii*) Find out the solubility of NaCl in the presence of C $CaCl_2$ solution?

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

C C 2C

Let solubility of NaCl in the presence of $CaCl_2$ solution is S' mol L^{-1}.

$NaCl \rightleftharpoons Na+ + Cl^-$

S' S' S' + 2C

According to L.M.A.

$K_{sp} = [Na^+]'[Cl^-]'$

$K_{sp} = S'(S' + 2C) = S'^2 + 2S'C$

(Neglecting the higher power terms of S')

$$\boxed{S' = \frac{K_{sp}}{2C}}$$

- Condition of precipitation

(*i*) $K_{sp} > K_{ip}$ ⇒ Unsaturated ⎫ No precipitation
(*ii*) $K_{sp} = K_{ip}$ ⇒ Saturated ⎭
(*iii*) $K_{sp} < K_{ip}$ ⇒ Super saturated ⇒ precipitation

Train Your Brain

Example 40: At 25°C what will be the solubility of silver carbonate in 0.1 M Na_2CO_3 solution? At this temperature K_{sp} of silver carbonate is 4×10^{-13}:

(*a*) 2×10^{-7} (*b*) 2×10^{-6} (*c*) 10^{-6} (*d*) 10^{-7}

Sol. (*b*) Let solubility = x moles/litres

$Ag_2CO_3 \longrightarrow 2Ag^+ + CO_3^{2-}$

x 2x x

$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}$

0.1 0.2 0.1

$K_{sp} = [Ag^+]^2[CO_3^{2-}]$

$[Ag^+] = 2x$

$[CO_3^{2-}] = 0.1 + x$

Credit:--- Divansh.....

$K_{sp}(Ag_2CO_3) = 4 \times 10^{-13}$

$K_{sp} = (2x)^2(0.1 + x)$

$4 \times 10^{-13} = (2x)^2(0.1 + x)$

$x << 0.1$

$4 \times 10^{-13} = 0.4x^2$

So, $x = 10^{-6}$

Example 41: Calculate the solubility of silver phosphate (Ag_3PO_4) in 0.10M $AgNO_3$? ($K_{sp} = 1.1 \times 10^{-16}$)

(*a*) 0.10 M
(*b*) 4.1×10^{-15} M
(*c*) 1.1×10^{-15} M
(*d*) 1.1×10^{-13} M

Sol. (*d*) $Ag_3PO_4 \rightarrow 3Ag^+ + PO_4^{3-}$

$3s + 0.1 \quad S$

$AgNO_3 \rightarrow Ag^+ + NO_3^-$

0.1

$K_{sp} = (3s + 0.1)^3(s)$

$\& \; 3s + 0.1 \approx 0.1$

$1.1 \times 10^{-16} = 10^{-3} \times s$

$$s = \frac{1.1 \times 10^{-16}}{10^{-3}} = 1.1 \times 10^{-13}$$

Example 42: At 30°C the solubility of Ag_2CO_3 ($K_{SP} = 8 \times 10^{-12}$) would be greatest in one litre of:

(*a*) 0.05 M Na_2CO_3
(*b*) 0.05 M $AgNO_3$
(*c*) Pure water
(*d*) 0.05 M K_2CO_3

Sol. (*c*) Presence of common ion decrease the solubility of salt. So solubility is maximum when there are no common ions i.e. in pure water.

Concept Application

54. Let the solubility of AgCl in pure water, in 0.01 M $CaCl_2$, in 0.01 M NaCl and in 0.05 M $AgNO_3$ be s_1, s_2, s_3 and s_4 respectively. Which of the following relations between these quantities is correct:

(*a*) $s_1 > s_2 > s_3 > s_4$
(*b*) $s_1 > s_2 = s_3 > s_4$
(*c*) $s_4 > s_2 > s_3 > s_1$
(*d*) $s_1 > s_3 > s_2 > s_4$

55. Ksp of AgCl is 1×10^{-10}. Its solubility in 0.1 M KNO_3 will be:

(*a*) 10^{-5} moles/litre
(*b*) $> 10^{-5}$ moles/litre
(*c*) $< 10^{-5}$ moles/litre
(*d*) None of these

56. Solubility of AgCl [$K_{sp} = 1 \times 10^{-10}$] in 0.2 M $AgNO_3$ and 0.2 M NaCl solution will be respectively:

(*a*) 5×10^{-10} M and 2×10^{-5} M
(*b*) 5×10^{-10} M and 5×10^{-10} M
(*c*) 2×10^{-5} M and 2×10^{-5} M
(*d*) 5×10^{-5} M and 5×10^{-5} M

57. The solubility of $PbSO_4$ in 0.01 M Na_2SO_4 solution is (K_{sp} for $PbSO_4 = 1.25 \times 10^{-9}$)

(*a*) 1.25×10^{-7} mol L^{-1}
(*b*) 1.25×10^{-9} mol L^{-1}
(*c*) 1.25×10^{-10} mol L^{-1}
(*d*) 1.25×10^{-18} mol L^{-1}

MINDFUL LISTENING GAME

- Sit with a friend or family member and listen to them share a story or experience without interrupting.
- Focus on their words, emotions, and body language. Reflect on how it feels to give someone your undivided attention.

Aarambh (Solved Examples)

1. For the reaction $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$ the equilibrium constant, K_C at 25°C is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which is originally 0.10 M in KCN and 0.03 M in $AgNO_3$.

Sol. For the complex forming reaction

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

$$K_c' = \frac{[[Ag(CN)_2]^-]}{[Ag^+][CN^-]^2} = \frac{1}{K_c} = 0.25 \times 10^{19}$$

Very high value of K_C' shows that complex formula equilibrium is spontaneous and almost all the Ag^+ ion would have reacted, leaving xM in solution. Thus,

	Ag^+	+	$2CN^-$	$\rightleftharpoons$	$[Ag(CN)_2]^-$
Initially	0.03 M		0.1 M		0
At equilibrium	xM		$(0.1 - 0.03 \times 2)$M		0.03 M

Putting these values in E.q. (i)

$$K_c' = 0.25 \times 10^{19} = \frac{(0.03)}{(x)(0.1 - 0.03 \times 2)^2}$$

$$\therefore x = [Ag^+] = 7.5 \times 10^{-18} M$$

2. $COCl_2$ gas dissociates according to the equation.

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

when heated to 724K; density of the gas mixture at 101.325 kPa and at equilibrium is 1.162 g dm^{-3}. Calculate (*a*) the degree of dissociation, (*b*) K_p (*c*) $\Delta G°$ for the reaction at 724 K.

Sol.

	$COCl_2(g)$	$\rightleftharpoons$ $CO(g)$	+ $Cl_2(g)$
Initially (mole)	1	0	0
At equilibrium	$(1 - x)$	x	x
Mole fraction	$\left(\frac{1-x}{1+x}\right)$	$\frac{x}{(1+x)}$	$\frac{x}{(1+x)}$
Partial pressure	$P\left(\frac{1-x}{1+x}\right)$	$\frac{Px}{(1+x)}$	$\frac{Px}{(1+x)}$

$$\text{Thus, } K_p = \frac{P_{CO} \cdot P_{Cl_2}}{P_{COCl_2}} = \frac{Px^2}{(1-x^2)} \qquad \text{...(i)}$$

$$\text{Also } P = \frac{\rho RT}{M(\text{observed})} (\rho = \text{density})$$

This gives observed molar mass of $COCl_2$.

$$= \frac{\rho RT}{P} = \frac{1.162 \times 0.0821 \times 724}{1} = 69 \text{ g mol}^{-1}$$

[ρ(density) g/dm^3 = kg/m^3] P = 101.325 kPa = 1 atm

(*a*) Using equation $x = \frac{D-d}{d} = \frac{99-69}{69} = 0.435$

[Note that $VD = \frac{\text{Molar Mass}}{2}$]

(*b*) Hence, from (i) $K_p = \frac{Px^2}{(1-x^2)} = \frac{1(0.435)^2}{[1-(0.435)^2]}$

$\therefore K_p = 0.233$

(*c*) $\Delta G° = -2.303 \, RT \log K_p$

$= -2.303 \times 8.314 \times 724 \log 0.233$

$= 8770 \text{ J mol}^{-1}$

3. Pure phosgene gas ($COCl_2$), 3.00×10^{-2} mol, was placed in a 1.50 L container. It was heated to 800 K, and at equilibrium pressure of CO was found to be 0.497 atm. Calculate the equilibrium constant K_p for the reaction.

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

Sol. Initial mol of $COCl_2(g)$ = 0.03 mol

Equilibrium pressure of CO(g) = 0.497 atm

$\therefore$ Number of moles of CO(g) at equilibrium

$$= \frac{PV}{RT} = \frac{0.497 \times 1.5}{0.0821 \times 800} = 0.0114 \text{ mol}$$

$$\underset{0.03-0.0114}{COCl_2(g)} \rightleftharpoons \underset{\substack{0 \\ +0.0114}}{CO(g)} + \underset{\substack{0 \\ 0.0114}}{Cl_2(g)}$$

$$K_c = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{\left(\frac{0.0114}{1.5}\right)\left(\frac{0.0114}{1.5}\right)}{\left(\frac{0.0186}{1.5}\right)} = 4.66 \times 10^{-3}$$

$K_p = K_c(RT)^{\Delta n} = 4.66 \times 10^{-3} \times (0.0821 \times 800) = 0.306$

For the reaction

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

$$K_p' = \frac{1}{K_p} = \frac{1}{0.306} = 3.27$$

4. Following equilibrium is studied by taking 1 mol of N_2 and 3 mol of H_2 in 1 L flask at a given temperature:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$NH_3(g)$ formed at equilibrium is neutralised by 100 mL of 1 M HCl. Calculate equilibrium constant K_c.

Sol. $NH_3(g) + HCl(aq) \rightleftharpoons NH_4Cl(aq)$

1 mol of NH_3 = 1 mol of HCl

0.1 mol of NH_3 = 0.1 mol of HCl

100 mL of 1 M HCl ≡ 100 millimole of HCl

≡ 0.1 mol of HCl = 0.1 mol NH_3

	$N_2(g)$	+ $3H_2(g)$	$\rightleftharpoons$ $2NH_3(g)$
Initial :	1	3	0
At eq	$(1-x)$	$(3-3x)$	$2x$

Thus, $2x = 0.1 \therefore x = 0.05$ mol, V = 1 L flask

Credit:--- Divansh.....

$$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}=\frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3}=\frac{4x^2V^2}{27(1-x)^4}=\frac{4\times(0.05)^2}{27(0.95)^4}$$

$K_C = 0.00045$

5. For the reaction, $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, calculate the equilibrium constant at 298 K. Given that the values of $\Delta H°$ and $\Delta S°$ of the reaction at 298 K are 77.2 kJ mol^{-1} and 122 JK^{-1} mol^{-1}.

Sol. Using the relation, $\Delta G° = \Delta H° - T\Delta S°$

$= 77200 - 298 \times 122$

$= 40844$ J mol^{-1}

Let the equilibrium constant be K_{eq}. We know that,

$\Delta G° = -2.303\ RT \log K_{eq}$

$$\text{or} \log K_{eq}=\frac{\Delta G°}{2.303\times 8.134\times 298}=-\frac{40844}{2.303\times 8.314\times 298}=-7.158$$

$K_{eq} = 6.95 \times 10^{-8}$

6. The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.

Sol. $N_2O_4 \rightleftharpoons 2NO_2(g)$

Mol. mass of $N_2O_4 = (28 + 64) = 92$

Vapour density, $D=\frac{92}{2}=46$

Let the degree of dissociation be x

Given, d = 30

Applying the relationship,

$$x=\frac{D-d}{d}=\frac{(46-30)}{30}=\frac{16}{30}=0.533$$

Degree of dissociation = 53.3%

7. N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C.

Sol. (i)

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
Initial	1	0
At equilibrium	$(1-x)$	$2x$

Total moles $= (1-x) + 2x = (1+x)$

$$P_{N_2O_4}=\left(\frac{1-x}{1+x}\right)P,\ P_{NO_2}=\frac{2x}{(1-x)}.P$$

Given x = 0.25 and P = 1 atm

$$P_{N_2O_4}=\left(\frac{1-0.25}{1+0.25}\right)\times 1=0.6\,\text{atm}$$

$$P_{NO_2}=\left(\frac{2\times 0.25}{1+0.25}\right)\times 1=0.4\ \text{atm}$$

$$K_p=\frac{(P_{NO_2})^2}{P_{N_2O_4}}=\frac{0.4\times 0.4}{0.6}=0.267\ \text{atm}$$

(ii) Let the degree of dissociation of N_2O_4 at 0.1 atm be 'α' then,

$$P_{N_2O_4}=\left(\frac{1-\alpha}{1+\alpha}\right)\times 0.1 \text{ and } P_{NO_2}=\frac{2\alpha}{(1+\alpha)}\times 0.1$$

$$K_p=\frac{\left(\frac{2\alpha}{1+\alpha}\right)^2\times(0.1)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)\times 0.1}=\frac{4\alpha^2\times 0.1}{(1-\alpha)(1+\alpha)}=\frac{0.4\alpha^2}{(1-\alpha^2)}$$

$$\text{or } 0.267=\frac{0.4\alpha^2}{1-\alpha^2} \text{ or } 0.667=\frac{\alpha^2}{1-\alpha^2}$$

$\Rightarrow \alpha = 0.632$

Hence, dissociation of $N_2O_4 = 63.2\%$

8. Calculate the S^{2-} ion concentration in a saturated solution (0.1 M) of H_2S whose pH was adjusted to 2 by the addition of HCl. ($K_a = 1.1 \times 10^{-21}$)

Sol. $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_a=\frac{[H^+]^2[S^{2-}]}{[H_2S]} \quad \text{or, } [S^{2-}]=\frac{K_a[H_2S]}{[H^+]^2}$$

pH = 2; so, $[H^+] = 1 \times 10^{-2}$ M

H_2S is a weak electrolyte, so, $[H_2S] = 0.1$ M

$[S^{2-}] = 1.1 \times 10^{-18}$ M

9. How many moles of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01 g formula mass of NaCN? K_a for HCN $= 4.1\times 10^{-10}$

Sol. Let a mole of HCl be added. It will combine with NaCN to form HCN.

$NaCN + HCl \rightarrow NaCl + HCN$

$[NaCN] = (0.01 - a)$

$[HCN] = a$

Applying the equation,

$$pH=\log\frac{[NaCN]}{[HCN]}-\log K_a$$

$$8.5=\log\frac{0.01-a}{a}-\log 4.1\times 10^{-10}$$

$$\text{So, } \log\frac{(0.01-a)}{a}=8.5+0.6128-10.0=(-0.8872)$$

$$\frac{(0.01-a)}{a}=0.1296$$

$$\text{or } a=\frac{0.01}{1.1296}=0.0089\,\text{mole}$$

10. A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.

Sol. $\underset{\text{Weak}}{HA}+\underset{\text{Strong}}{BOH} \rightleftharpoons BA + H_2O$

$HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$

or $HA + OH^- \rightleftharpoons A^- + H_2O$

$$K=\frac{[A^-]}{[HA][OH^-]}$$

In the above reaction

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

So, $K = \frac{1}{K_h}$

We know that,

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.0 \times 10^{-4}} = 10^{-10} \Rightarrow K = 10^{10}$$

11. The solubility product of $Ca(OH)_2$ at 25°C is 4.42×10^{-5} $mole^3$ $litre^{-3}$. A 500ml of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4M NaOH solution. How much $Ca(OH)_2$ in milligrams is precipitated?

Sol. $K_{sp}(Ca(OH)_2) = 4.42 \times 10^{-5}$ mol^3 l^{-3}

For a saturated solution, $4s^3 = 4.42 \times 10^{-5}$

$s = 2.23 \times 10^{-2} = 0.0223\ M = [Ca^{+2}]$

$[OH^-] = 2s = 0.0446\ M$

Now, $\frac{500 \times 0.0446 + 500 \times 0.4}{1000} = [OH^-]_{new} = 0.2223$

$[Ca^{2+}][OH^-]^2_{new} = 4.42 \times 10^{-5}$

$[Ca^{2+}]_{remaining} = 8.94 \times 10^{-4}$

$[Ca^{2+}]_{original} = 0.0223 \times \frac{500}{1000} = 111.5 \times 10^{-4}$

$\therefore$ ppt $= 111.5 \times 10^{-4} - 8.94 \times 10^{-4} = 102.56 \times 10^{-4}$

MW $[Ca(OH)_2] = 74g$

wt. in mg $= 102.56 \times 10^{-4} \times 74 \times 10^3 = 758.9$ mg

12. The solubility product of $BaSO_4$ and $BaCrO_4$ at 25°C are 1×10^{-10} and 2.4×10^{-10} respectively. Calculate the simultaneous solubilities of $BaSO_4$ and $BaCrO_4$.

Sol. Solubility of $BaSO_4 = x$

Solubility of $BaCrO_4 = y$

$(x + y).\ x = 10^{-10}$

$(x + y).\ y = 2.4 \times 10^{-10} \Rightarrow y = 2.4\ x$

$\therefore (x + 2.4x).x = 10^{-10}$

$3.4x^2 = 10^{-10}$

$\Rightarrow x = 5.42 \times 10^{-6}$ M

$y = 1.3 \times 10^{-5}$ M

13. Calculate change in pH of 1 L buffer solution containing 0.10 Mole each of NH_3 and NH_4Cl upon addition of

(*i*) 0.02 mole of dissolved gaseous HCl.

(*ii*) 0.02 mole of dissolved NaOH. (Assuming volume to be constant). $K_b(NH_3) = 1.8 \times 10^{-5}$

Sol. (*i*)

$$\begin{array}{ccccc} NH_3 & + & HCl & \rightarrow & NH_4Cl \\ 0.1-0.02 & & 0.02 & & 0.02 \end{array}$$

Net $NH_4Cl = 0.1 + 0.02 = 0.12$

Net $NH_3 = 0.08$

$$\Delta pH = \log\frac{[salt]}{[base]} = \log\frac{0.12}{0.08} = 0.1761$$

(*ii*) Same as above, $\Delta pH = 0.1761$

14. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution, should be mixed with 10ml sample of blood, which is 2 M in H_2CO_3 in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is $= 7.8 \times 10^{-7}$.

Sol. $pH = pk_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$

$$7.4 = 7 - \log 7.8 + \log\left(\frac{5V}{20}\right)$$

$\Rightarrow V = 78$ mL

15. Calculate the amount of NH_4Cl required to be dissolved in 500 ml water to have pH = 4.5 [k_b for $NH_4OH = 1.8 \times 10^{-5}$].

Sol. $[H^+] = 10^{-pH} = 10^{-4.5} = 3.162 \times 10^{-5}$ M

$$K_h = Ch^2 = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$h = \frac{K_h}{Ch} = \frac{K_h}{[H^+]} = \frac{5.5 \times 10^{-10}}{3.162 \times 10^{-5}} = 1.74 \times 10^{-5}$$

$$C = \frac{[H^+]}{h} = \frac{3.162 \times 10^{-5}}{1.74 \times 10^{-5}} = 1.8\ mol/L$$

500 ml of H_2O contains $\frac{1.8}{2} = 0.9$ mole of NH_4Cl

Mass in NH_4Cl gm $= 0.9 \times 53.5 = 48.15$ g

16. Calculate the pH of each of the following solutions

(*a*) 100 ml of 0.1 M CH_3COOH mixed with 100 ml of 0.1 M NaOH.

(*b*) 100 ml of 0.1 M CH_3COOH mixed with 50 ml of 0.1 M NaOH.

(*c*) 50 ml of 0.1 M CH_3COOH mixed with 100 ml of 0.1 M NaOH. ($pK_a(CH_3COOH) = 9.75$)

Sol. (*a*)

$$\underset{1mole}{CH_3COOH} + \underset{1mole}{NaOH} \rightarrow \underset{1mole}{CH_3COONa} + \underset{1mole}{H_2O}$$

m. moles of $CH_3COOH = 0.1 \times 100 = 10$

m. moles of NaOH $= 100 \times 0.1 = 10$

Therefore, m. moles of CH_3COONa formed is 10

Now in the solution, only salt CH_3COONa is present, therefore, pH of solution can be calculated by the hydrolysis of CH_3COONa

CH_3COONa is a salt of weak acid with strong base

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2} \times 4.75 + \frac{1}{2}\log\left(\frac{10}{200}\right)$$

$= 8.72$

Credit:--- Divansh.....

(*b*)

	CH_3COOH	+ $NaOH$ →	CH_3COONa	+ H_2O
Initial m. mole	10	5	0	0
m. moles after reaction	10–5	0	5	5

Since in the solution, mixture of CH_3COOH and CH_3COONa is present, therefore, solution is an acidic buffer and pH can be calculated as

$$pH = pK_a + \log\frac{[salt]}{[acid]}, pH = 4.75 + \log\left(\frac{\frac{5}{150}}{\frac{5}{150}}\right)$$

$$\boxed{pH = 4.75}$$

(*c*)

	CH_3COOH	+ $NaOH$ →	CH_3COONa	+ H_2O
Initial m. mole	5	10	0	0
m. moles after reaction	0	(10–5)	5	5

Now in the solution strong base NaOH and salt of weak acid with strong base is present. We can assume that OH^- ions concentration from the hydrolysis of salt is negligible because hydrolysis of CH_3COONa is suppressed by the presence of string base NaOH.

$$\underset{\text{(from salt)}}{CH_3COO^-} + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$\therefore [HO^-] = \left[\frac{5}{150}\right] = \left(\frac{1}{30}\right)$$

$$pOH = -\log[OH^-] = -\log\left(\frac{1}{30}\right) = \log 30 = 1.4771$$

$$pH + pOH = 14$$

$$pH = 14 - 1.47771 = 12.52$$

17. The equilibrium constant for the decomposition of water $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ is given by: (α = degree of dissociation of H_2O (g); p = Total equilibrium pressure)

(*a*) $K = \frac{\alpha^2 p^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$ (*b*) $K = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(*c*) $K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}}$ (*d*) $K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

Sol.

$H_2O(g)$	→ $H_2(g)$	+ $\frac{1}{2}O_2(g)$
1	0	0
1 − α	α	α/2

Total moles at equilibrium = 1 − α + α + (α/2) = 1 + (α/2)

Let the total pressure at equilibrium be = p

So, $p_{H_2O} = \frac{1-\alpha}{1+(\alpha/2)} \times p$

$$p_{H_2} = \frac{\alpha}{1+(\alpha/2)} \times p$$

$$p_{O_2} = \frac{(\alpha/2)}{1+(\alpha/2)} \times p$$

$$\text{So, } K_p = \frac{(p_{O_2})^{1/2}(p_{H_2})}{(p_{H_2O})}$$

$$= \frac{\left(\frac{\alpha/2}{1+(\alpha/2)} \times p\right)^{1/2}\left(\frac{\alpha}{1+(\alpha/2)} \times p\right)}{\left(\frac{1-\alpha}{1+(\alpha/2)}\right)p}$$

$$K_p = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

Therefore, option (*d*) is the correct answer.

> *"Mindfulness is the pause between stimulus and response."*
>
> **– Viktor Frankl**

School Level Problems

1. A reaction reaches a state of equilibrium only when:
   - (*a*) The reactants and products stop reacting
   - (*b*) The concentration of reactants and products become equal
   - (*c*) The products react together at the same rate at which they are formed
   - (*d*) All the reactants and products are in the same state of matter

2. For the equilibrium,

   $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

   K_p is related to K_c by the reaction:
   - (*a*) $K_p = K_c(RT)$
   - (*b*) $K_p = K_c(RT)^2$
   - (*c*) $K_p = \frac{K_c}{RT}$
   - (*d*) $K_p = \frac{K_c}{(RT)^2}$

3. Two moles of each reactants A and B are taken in the reaction flask. They react in the following manner,

   $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

   At equilibrium, it was found that the concentration of "C" is triple that of B. The equilibrium constant for the reaction is:
   - (*a*) 4.5
   - (*b*) 6
   - (*c*) 9
   - (*d*) 1/6

4. Predict the effect of increased pressure on the following reaction's equilibrium.

   $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
   - (*a*) Equilibrium shift to the right
   - (*b*) Equilibrium shift to the left
   - (*c*) No effect on equilibrium
   - (*d*) Reaction stops

5. In the reaction $NH_3 + H_2O \rightleftharpoons NH^+_4 + OH^-$, the conjugate acid-base pair is
   - (*a*) NH_3 and H_2O
   - (*b*) NH_3 and OH^-
   - (*c*) H_2O and NH^+_4
   - (*d*) NH^+_4 and NH_3

6. What is the pH at equivalence point in the titration of 0.1M CH_3COOH and 0.1 M NaOH?

   (K_a for acetic acid is 1.8×10^{-5})
   - (*a*) 7
   - (*b*) Between 7 and 8
   - (*c*) Between 8 and 9
   - (*d*) Between 6 and 7

7. A certain buffer solution contains equal concentration of X^- and HX. The K_a for HX is 10^{-8}. The pH of buffer is:
   - (*a*) 3
   - (*b*) 8
   - (*c*) 11
   - (*d*) 14

8. Solubility product of a sparingly soluble salt AX_2 is 3.2×10^{-11}. Its solubility in mol/litre is:
   - (*a*) 5.6×10^{-6}
   - (*b*) 3.1×10^{-4}
   - (*c*) 2×10^{-4}
   - (*d*) 4×10^{-4}

ASSERTION AND REASON TYPE QUESTIONS

Directions: These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

- (*a*) Both Assertion and Reason are True and the Reason is a correct explanation of the Assertion.
- (*b*) Both Assertion and Reason are True but Reason is not a correct explanation of the Assertion.
- (*c*) Assertion is True but the Reason is False.
- (*d*) Assertion is False but Reason is True.

9. **Assertion:** For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

   Reason: Equilibrium constant is independent of temperature.

10. **Assertion:** K_p is related to K_c by the relation. $K_p = \frac{K_c[RT]}{\Delta n}$

    Reason: K_p has different dimensions as that of K_c

MATCH THE COLUMN TYPE QUESTIONS

11. Match the following species with the corresponding conjugate acid

	Species		Conjugate acid
A.	NH_3	(p)	CO_3^{2-}
B.	HCO_3^-	(q)	NH_4^+
C.	H_2O	(r)	H_3O^+
D.	HSO_4^-	(s)	H_2SO_4
		(t)	H_2CO_3

- (*a*) A-(t); B-(r); C-(q); D-(p)
- (*b*) A-(q); B-(t); C-(r); D-(s)
- (*c*) A-(q); B-(s); C-(t); D-(p)
- (*d*) A-(p); B-(t); C-(q); D-(r)

12. Match the Column-I with Column-II.

	Column-I Species		Column-II Conjugate acid
A.	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(p)	$\Delta n_g > 0$
B.	$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(q)	$K_p < K_c$
C.	$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$	(r)	K_p not defined
D.	$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons$ $CH_3COOH(l) + C_2H_5OH(l)$ (assume temperature = 25°C)	(s)	$K_p > K_c$

(*a*) A-(q); B-(p,s); C-(p,s); D-(r)

(*b*) A-(p,s); B-(q); C-(p,s); D-(r)

(*c*) A-(p,s); B-(r); C-(p); D-(p,s)

(*d*) A-(r); B-(p,s); C-(q); D-(p,s)

SHORT ANSWER TYPE QUESTIONS

13. Consider the dissociation of PCl_5,

$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

If α is the degree of dissociation at equilibrium pressure "P", then calculate the equilibrium constant K_p.

14. A weak monobasic weak acid solution has a molarity of 0.005 M and pH of 5. Calculate the percentage ionization of this solution.

15. The value of $K_c = 4.24$ at 800K for the reaction:

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Calculate equilibrium concentrations of CO_2, H_2, CO and H_2O at 800 K if only CO and H_2O are present initially at concentrations of 0.10 M each.

16. Calculate the molar solubility of $Ni(OH)_2$ in 0.20 M NaOH. The ionic product of $Ni(OH)_2$ is 2.0×10^{-15}.

17. You are given a weak acid, acetic acid (CH_3COOH), with a pK_a of 4.76. Calculate the pH of a buffer solution prepared by mixing 50.0 mL of 0.20 M acetic acid with 50.0 mL of 0.10 M sodium acetate (CH_3COONa).

18. Calculate the solubility of lead(II) iodide (PbI_2) in a solution that contains 0.2 M potassium iodide (KI). Given the solubility product constant (K_{sp}) for PbI_2 is 7.1×10^{-9}.

LONG ANSWER TYPE QUESTIONS

19. (i) The decomposition of dinitrogen pentoxide (N_2O_5) in the gas phase follows the equation:

$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$

At a certain temperature, the initial concentration of N_2O_5 is 0.2 M. After a certain time, it is found that the concentration of N_2O_5 has decreased to 0.1 M. Calculate the equilibrium concentrations of NO_2 and O_2 and the equilibrium constant (K_c) for the reaction.

(ii) How does changing the temperature affect the equilibrium constant (K_c) for an endothermic and an exothermic reaction? Provide examples.

20. (i) Explain how a buffer solution resists changes in pH when small amounts of acid or base are added to it. Use the Henderson-Hasselbalch equation to illustrate the relationship between the ratio of $[A^-]/[HA]$ and the pH of a buffer solution.

(ii) You are given a solution containing 0.1 M acetic acid (CH_3COOH) and 0.1 M sodium acetate (CH_3COONa). Calculate the pH of this buffer solution. Given that the pK_a of acetic acid is 4.76.

21. Define the common ion effect and explain how it influences the solubility of a sparingly soluble salt in a solution containing a common ion. Use an example to support your explanation.

22. Explain:

(i) The ionization of HCl in in water is given below as:

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Mention two conjugate acid-base pairs in the above ionization.

(ii) An aqueous solution of sugar does not conduct electricity but on addition of sodium chloride to water, it begins to conduct electricity. Explain.

(iii) Arrange the given below conjugate bases in decreasing order of basic strength:

OH^-, RO^-, CH_3COO^-, Cl^-

23. (i) Consider the reaction $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, which has a solubility product constant (K_{sp}) of 1.8×10^{-10}. Calculate the molar solubility of AgCl in water and determine the concentration of Ag^+ and Cl^- ions in a saturated AgCl solution. Show the necessary calculations.

(ii) Explain the concept of the common ion effect and its impact on the solubility of salts. How does the presence of a common ion affect the solubility product equilibrium?

(iii) Magnesium is not precipitated from a solution of its salt by NH_4OH in the presence of NH_4Cl. Explain.

CASE STUDY BASED QUESTIONS

24. Consider the following reversible reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

A closed container initially contains N_2, H_2, and NH_3 at equilibrium. The system is then subjected to different changes. Analyze each scenario and determine the resulting shift in the equilibrium position based on Le Chatelier's principle.

(i) If the volume of the container is decreased by half, what will be the effect on the equilibrium position?

(*a*) The equilibrium will shift towards more N_2 and H_2.

(*b*) The equilibrium will shift towards more NH_3.

(*c*) The equilibrium will remain unchanged.

(*d*) The equilibrium will shift towards more NH_3 and less N_2 and H_2.

(ii) If the temperature of the system is increased, what will be the effect on the equilibrium position?

(*a*) The equilibrium will shift towards more N_2 and H_2.

(*b*) The equilibrium will shift towards more NH_3.

(*c*) The equilibrium will remain unchanged.

(*d*) The equilibrium will shift towards more NH_3 and less N_2 and H_2.

(iii) If more NH_3 is added to the container, what will be the effect on the equilibrium position?

(*a*) The equilibrium will shift towards more N_2 and H_2.

(*b*) The equilibrium will shift towards more NH_3.

(*c*) The equilibrium will remain unchanged.

(*d*) The equilibrium will shift towards more NH_3 and less N_2 and H_2.

(iv) If a catalyst is added to the system, what will be the effect on the equilibrium position?

(*a*) The equilibrium will shift towards more N_2 and H_2.

(*b*) The equilibrium will shift towards more NH_3.

(*c*) The equilibrium will remain unchanged.

(*d*) The equilibrium will shift towards more NH_3 and less N_2 and H_2.

> *"Mindfulness is like a muscle—the more you practice, the stronger it gets."*

Prarambh (Topicwise)

CHEMICAL EQUILIBRIUM

Properties of equilibrium, active mass, homogeneous & heterogeneous equilibrium (theoretical)

1. In chemical reaction $A \rightleftharpoons B$, the system will be known in equilibrium when
   (*a*) A completely changes to B
   (*b*) 50% of A changes to B
   (*c*) The rate of change of A to B and B to A on both the sides are same
   (*d*) Only 10% of A changes to B

2. The active mass of 64 gm of HI in a two litre flask would be
   (*a*) 2 (*b*) 1 (*c*) 5 (*d*) 0.25

3. Theory of 'active mass' indicates that the rate of chemical reaction is directly proportional to the
   (*a*) Equilibrium constant (*b*) Properties of reactants
   (*c*) Volume of apparatus (*d*) Concentration of reactants

4. Which of the statement is false?
   (*a*) The greater the concentration of the substances involved in a reaction, the lower the speed of the reaction.
   (*b*) The point of dynamic equilibrium is reached when the reaction rate in one direction just balances the reaction rate in the opposite direction.
   (*c*) The dissociation of weak electrolyte is a reversible reaction.
   (*d*) All of these

HOMOGENEOUS EQUILIBRIUM: K_C

5. For the system $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant is
   (*a*) $\frac{[3A][2B]}{[C]}$ (*b*) $\frac{[3C]}{[3A][2B]}$
   (*c*) $\frac{[A]^3[B]^2}{[C]}$ (*d*) $\frac{[C]}{[A]^3[B]^2}$

6. 4 moles of A are mixed with 4 moles of B. At equilibrium for the reaction $A+B \rightleftharpoons C+D$, 2 moles each of C and D are formed. The equilibrium constant for the reaction will be
   (*a*) $\frac{1}{4}$ (*b*) $\frac{1}{2}$
   (*c*) 1 (*d*) 4

7. For the system $A(g) + 2B(g) \rightleftharpoons C(g)$, the equilibrium concentrations of [A] = 0.06 mole/litre, [B] = 0.12 mole/litre, [C] = 0.216 mole/litre. The K_{eq} for the reaction is
   (*a*) 250 (*b*) 416 (*c*) 4×10^{-3} (*d*) 125

8. Partial pressures (in atm) of A, B, C and D on the basis of gaseous system $A + 2B \rightleftharpoons C + 3D$ are A = 0.20; B = 0.10; C = 0.30 and D = 0.50. The numerical value of equilibrium constant is
   (*a*) 11.25 (*b*) 18.75
   (*c*) 5 (*d*) 3.75

9. 2 moles of PCl_5 were heated in a closed vessel of 2 litre capacity. At equilibrium, 40% of PCl_5 is dissociated into PCl_3 and Cl_2. The value of equilibrium constant is
   (*a*) 0.266 (*b*) 0.53
   (*c*) 2.66 (*d*) 5.3

10. Unit of equilibrium constant for the reversible reaction is $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
    (*a*) mol^{-1} litre (*b*) mol^{-2} litre
    (*c*) mol $litre^{-1}$ (*d*) None of these

HOMOGENEOUS EQUILIBRIUM: K_P

11. At 3000 K, the equilibrium pressures of CO_2, CO and O_2 are 0.6,0.4 and 0.2 atmosphere respectively. K_p for the reaction, $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ is
    (*a*) 0.089 (*b*) 0.0533
    (*c*) 0.133 (*d*) 0.177

12. For the reaction: $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$, if the initial concentration of $[H_2] = [CO_2] = 1$ and x moles/litre of hydrogen is consumed at equilibrium, the correct expression of K_p is
    (*a*) $\frac{x^2}{(1-x)^2}$ (*b*) $\frac{(1+x)^2}{(1-x)^2}$
    (*c*) $\frac{x^2}{(2+x)^2}$ (*d*) $\frac{x^2}{1-x^2}$

13. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressure of CO_2 and CO are 2.0 and 4.0 atm respectively at equilibrium. The equilibrium constants for the reaction is
    (*a*) 0.5 (*b*) 4.0
    (*c*) 8.0 (*d*) 32.0

14. For the equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, which of the following expression is correct?
    (*a*) $K_p = \left(P_{CaO} + P_{CO_2} / P_{CaCO_3}\right)$
    (*b*) $K_p = P_{CO_2}$
    (*c*) $K_p = \left(P_{CaO} \times P_{CO_2}\right).P_{CaCO_3}$
    (*d*) $K_p = \frac{[CaO][CO_2]}{[CaCO_3]}$

RELATION BETWEEN K_p AND K_C, REACTION QUOTIENT AND ITS APPLICATIONS

15. In which of the following reaction, the value of K_p will be equal to K_C?

(*a*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(*b*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(*c*) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(*d*) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

16. The relation between equilibrium constant K_p and K_c is

(*a*) $K_c = K_p(RT)^{\Delta n_g}$ (*b*) $K_p = K_c(RT)^{\Delta n_g}$

(*c*) $K_p = \left(\frac{Kc}{RT}\right)^{\Delta n_g}$ (*d*) $K_p - K_c = (RT)^{\Delta n_g}$

17. For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$

(*a*) $K_p = K_c(RT)$ (*b*) $K_p = K_c(RT)$

(*c*) $K_p = K_c(RT)^{-2}$ (*d*) $K_p = K_c(RT)^{-1}$

18. For the reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

($K_c = 1.8 \times 10^{-6}$ at 184 °C), ($R = 0.0831$ kJ mol^{-1}K^{-1})

K_c and K_p are related to each other by

(*a*) K_p is greater than K_c

(*b*) K_p is less than K_c

(*c*) $K_p = K_c$

(*d*) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

19. The reaction between N_2 and H_2 to form ammonia has $K_c = 6 \times 10^{-2}$ at the temperature 500°C. The numerical value of K_p for this reaction is

(*a*) 1.5×10^{-5} (*b*) 1.5×10^{5}

(*c*) 1.5×10^{-6} (*d*) 1.5×10^{6}

20. In which of the following, the reaction proceeds towards completion?

(*a*) $K = 10^3$ (*b*) $K = 10^{-2}$

(*c*) $K = 10$ (*d*) $K = 1$

PROPERTIES OF EQUILIBRIUM CONSTANT

21. The equilibrium constant of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 64. If the volume of the container is reduced to one fourth of its original volume, the value of the equilibrium constant will be

(*a*) 16 (*b*) 32

(*c*) 64 (*d*) 128

22. A reversible chemical reaction has two reactants in equilibrium. If the concentrations of the reactants are doubled, then the equilibrium constant will

(*a*) Also be doubled

(*b*) Be halved

(*c*) Become one-fourth

(*d*) Remain the same

23. Two gaseous equilibrium $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ and $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ have equilibrium constants K_1 and K_2 respectively at 298 K. Which of the following relationships between K_1 and K_2 is correct?

(*a*) $K_1 = K_2$ (*b*) $K_2 = K_1^2$

(*c*) $K_2 = \frac{1}{K_1^2}$ (*d*) $K_2 = \frac{1}{K_1}$

24. Equilibrium constant for the synthesis of HI is 50. The value of equilibrium constant for dissociation of HI is

(*a*) 50 (*b*) 5 (*c*) 0.2 (*d*) 0.02

25. The equilibrium constant for the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is K and for the reaction the $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ equilibrium constant is K′. K and K′ will be related as

(*a*) $K = K'$ (*b*) $K' = \sqrt{K}$

(*c*) $K = \sqrt{K'}$ (*d*) $K \times K' = 1$

26. The equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is K, then the equilibrium constant for the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ is

(*a*) 1/K (*b*) $1/K^2$ (*c*) $\sqrt{K}$ (*d*) $\frac{1}{\sqrt{K}}$

27. For the gaseous phase reaction

$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $\Delta H° = +43.5$ kcal mol^{-1}

Which of the given statement is correct?

(*a*) K_c varies with addition of NO

(*b*) K_c decrease as temperature decreases

(*c*) K_c increases as temperature decreases

(*d*) K_c is independent of temperature

28. If for $H_2(g) + \frac{1}{2}S_2(s) \rightleftharpoons H_2S(g)$ and $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$.

The equilibrium constants are K_1 and K_2 respectively, the reaction $Br_2(g) + H_2S(g) \rightleftharpoons 2HBr(g) + \frac{1}{2}S_2(s)$ would have equilibrium constant

(*a*) $K_1 \times K_2$ (*b*) K_1/K_2

(*c*) K_2/K_1 (*d*) K_2^2/K_1

DEGREE OF DISSOCIATION (α) AND VAPOUR DENSITY

29. 5 moles of SO_2 and 5 moles of O_2 are allowed to react to form SO_3 in a closed vessel. At the equilibrium stage, 60% of SO_2 is used up. The total number of moles of SO_2, O_2 and SO_3 in the vessel at equilibrium is

(*a*) 10.0 (*b*) 8.5 (*c*) 10.5 (*d*) 3.9

Credit:--- Divansh.....

30. 9.2 grams of $N_2O_4(g)$ is taken in a closed one litre vessel and heated till the following equilibrium is reached $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At equilibrium, 50% $N_2O_4(g)$ is dissociated. What is the value of equilibrium constant (in mol $litre^{-1}$) (Molecular weight of $N_2O_4 = 92$)?

(*a*) 0.1 (*b*) 0.4 (*c*) 0.2 (*d*) 2

31. 3.2 moles of hydrogen iodide were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation at this temperature was found to be 22%. The number of moles of hydrogen iodide present at equilibrium are

(*a*) 2.496 (*b*) 1.87 (*c*) 2 (*d*) 4

32. The vapour density of completely dissociated NH_4Cl would be

(*a*) Slight less than half that of NH_4Cl
(*b*) Half that of NH_4Cl
(*c*) Double that of NH_4Cl
(*d*) Determined by the amount of solid NH_4Cl in the experiment

33. If % dissociation for reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 20% at 1 atm pressure. K_P for the given reaction is

(*a*) 0.04 (*b*) 0.05 (*c*) 0.07 (*d*) 0.06

HETEROGENEOUS EQUILIBRIUM

34. Some amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH_4HS decomposition at this temperature is

(*a*) 0.30 (*b*) 0.18 (*c*) 0.17 (*d*) 0.11

35. Some solid is placed in a flask containing 0.5 atm of NH_3, what would be pressures of NH_3 when equilibrium is reached?

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g),\ K_p = 0.11$$

(*a*) 6.65 atm (*b*) 0.165 atm
(*c*) 0.0665 atm (*d*) 66.5 atm

LE-CHATELIER'S PRINCIPLE

36. In the manufacture of ammonia by Haber's process,

$$N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g) + 92.3\,kJ$$

which of the following conditions is unfavourable?

(*a*) Increasing the temperature
(*b*) Increasing the pressure
(*c*) Reducing the temperature
(*d*) Removing ammonia as it is formed

37. For the reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, the position of equilibrium can be shifted to the right by

(*a*) Increasing the temperature
(*b*) Doubling the volume of vessel
(*c*) Addition of Cl_2 at constant volume
(*d*) Addition of equimolar quantities of PCl_3 and PCl_5

38. What is the effect of halving the pressure by doubling the volume on the following system at 500°C?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(*a*) Shift to product side
(*b*) Shift to product formation
(*c*) Liquefaction of HI
(*d*) No effect

39. In equilibrium,

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The equilibrium constant may change when

(*a*) CH_3COO^- are added
(*b*) CH_3COOH is added
(*c*) Catalyst is added
(*d*) Mixture is heated

40. In the reaction $A_2(g) + 4B_2(g) \rightleftharpoons 2AB_4(g),\ \Delta H < 0$ the formation of AB_4 will be favoured at

(*a*) Low temperature, high pressure
(*b*) High temperature, low pressure
(*c*) Low temperature, low pressure
(*d*) High temperature, high pressure

41. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - Qcals$

In the above reaction, which is the essential condition for the higher production of NO?

(*a*) High temperature
(*b*) High pressure
(*c*) Low temperature
(*d*) Low pressure

42. Which of the following reactions proceed in forward direction at low pressure?

(*a*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(*b*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(*c*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(*d*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

THERMODYNAMIC OF EQUILIBRIUM AND MISCELLANEOUS

43. For a system in equilibrium, $\Delta G = 0$ under conditions of constant

(*a*) Temperature and pressure
(*b*) Temperature and volume
(*c*) Energy and volume
(*d*) Pressure and volume

44. A reaction attains equilibrium when the free energy change accompanying it is

(*a*) Positive and large
(*b*) Zero
(*c*) Negative and large
(*d*) Negative and small

Credit:--- Divansh.....

IONIC EQUILIBRIUM

Acid Base Concept

45. Review the following equilibrium and choose the correct statement.

$$HClO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_4^-(aq)$$

(a) $HClO_4$ is the conjugate acid of H_2O
(b) H_3O^+ is the conjugate base of H_2O
(c) H_2O is the conjugate acid of H_3O^+
(d) ClO_4^- is the conjugate base of $HClO_4$

46. Which of the following can act both as Bronsted acid and Bronsted base?
(a) Cl^- (b) HCO_3^- (c) H_3O^+ (d) OH^-

47. An example of a Lewis acid is
(a) NaCl (b) $MgCl_2$ (c) $AlCl_3$ (d) $SnCl_4$

48. With reference to protonic acids, which of the following statements is correct?
(a) PH_3 is more basic than NH_3.
(b) PH_3 is less basic than NH_3.
(c) PH_3 is equally basic as NH_3.
(d) PH_3 is amphoteric while NH_3 is basic.

49. Dissociation of H_3PO_4 takes place in following steps
(a) 1 (b) 2 (c) 3 (d) 4

50. The species which acts as a Lewis acid but not a Bronsted acid is
(a) NH_2^- (b) O^{2-} (c) BF_3 (d) OH^-

PROPERTIES OF WATER, pH SCALE, AUTOPROTOLYSIS

51. The unit of ionic product of water, K_w is
(a) $Mol^{-1} L^{-1}$ (b) $Mol^{-2} L^{-2}$
(c) $Mol^{-2} L^{-1}$ (d) $Mol^2 L^{-2}$

52. At 90°C, pure water has $[H_3O^+] = 10^{-6}$. The value of K_w at this temperature will be
(a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8}

53. The pH of 1N H_2O is
(a) 7 (b) >7 (c) <7 (d) 0

54. In the equilibrium:

$$CH_3COOH(aq) + HF(aq) \rightleftharpoons CH_3COOH_2^+(aq) + F^-(aq)$$

(a) F^- is the conjugate acid of CH_3COOH
(b) F^- is the conjugate base of HF
(c) CH_3COOH is the conjugate acid of $CH_3COOH_2^+$
(d) $CH_3COOH_2^+$ is the conjugate base of CH_3COOH

55. Which of the following is a conjugated acid-base pair?
(a) HCl, NaOH (b) NH_4Cl, NH_4OH
(c) H_2SO_4, HSO_4^- (d) KCN, HCN

56. The conjugate acid of HPO_4^{2-} is
(a) H_3PO_4 (b) H_3PO_3 (c) $H_2PO_4^-$ (d) PO_4^{3-}

57. The conjugate acid of NH_2^- is
(a) NH_3 (b) NH_4^+ (c) NH_2OH (d) PO_4^{3-}

58. Among the following, the weakest base is
(a) H^- (b) CH_3^- (c) CH_3O^- (d) Cl^-

pH CALCULATION

59. Aqueous solution of HCl has the pH = 4. Its molarity would be
(a) 4 M (b) 0.4 M
(c) 0.0001 M (d) 10 M

60. What is the pH value of $\frac{N}{1000}$ KOH solution?
(a) 10^{-11} (b) 3 (c) 2 (d) 11

61. pH + pOH is equal to (at 25°C)
(a) Zero (b) Fourteen
(c) A negative number (d) Infinity

62. Which one of the following solution has pH 12?
(a) 0.01M KOH (b) 1N KOH
(c) 1N NaOH (d) 1N $Ca(OH)_2$

63. pH values of HCl and NaOH solutions each of strength $\frac{N}{100}$ will be respectively
(a) 2 and 2 (b) 2 and 12
(c) 12 and 2 (d) 2 and 10

64. What will be the pH of a 10^{-8} M HCl solution?
(a) 8.0 (b) 7.0 (c) 6.98 (d) 14.0

65. pH of completely dissociated 0.005 M H_2SO_4 is
(a) 3 (b) 4 (c) 2 (d) 5

66. The pH of a 0.02 M solution of hydrochloric acid is
(a) 2.0 (b) 1.7 (c) 0.3 (d) 2.2

67. NaOH(aq), HCl(aq) and NaCl(aq) concentration of each is 10^{-3} M. Their pH will be, respectively
(a) 10, 6, 2 (b) 11, 3, 7 (c) 10, 2, 6 (d) 3, 4, 7

68. The pH of a 10^{-10} molar HCl solution is approximately
(a) 10 (b) 7 (c) 1 (d) 14

69. Electrolytes when dissolved in water dissociate into their constituent ions. The degree of dissociation of an electrolyte increases with
(a) Increasing concentration of the electrolyte
(b) Decreasing concentration of the electrolyte
(c) Decreasing temperature
(d) Presence of a substance yielding a common ion

70. A monoprotic acid in 1.00 M solution is 0.01% ionised. The dissociation constant of this acid is
(a) 1×10^{-8} (b) 1×10^{-4}
(c) 1×10^{-6} (d) 10^{-5}

71. Which one is strongest electrolyte out of the following?
(a) NaCl (b) CH_3COOH
(c) NH_4OH (d) $C_6H_{12}O_6$

Credit:--- Divansh.....

72. If α is the degree of ionization, C is the concentration of a weak electrolyte and K_a is the acid ionization constant, then the correct relationship between α, C and K_a is

(*a*) $\alpha^2 = \sqrt{\frac{K_a}{C}}$ (*b*) $\alpha^2 = \sqrt{\frac{C}{K_a}}$

(*c*) $\alpha = \sqrt{\frac{K_a}{C}}$ (*d*) $\alpha = \sqrt{\frac{C}{K_a}}$

73. The extent of ionization increases

(*a*) With the increase in concentration of solute

(*b*) On addition of excess water to solution

(*c*) On decreasing the temperature of solution

(*d*) On stirring the solution vigorously

74. For a weak acid HA, Ostwald's dilution law is represented by the equation

(*a*) $K_a = \frac{\alpha c}{1-\alpha^2}$ (*b*) $K_a = \frac{\alpha^2 c}{1-\alpha}$

(*c*) $\alpha = \frac{K_a c}{1-c}$ (*d*) $K_a = \frac{\alpha^2 c}{1-\alpha^2}$

75. Concentration of CN^- in 0.1 M HCN, is $[K_a = 4 \times 10^{-10}]$

(*a*) 2.5×10^{-6} M (*b*) 4.5×10^{-6} M

(*c*) 6.3×10^{-6} M (*d*) 9.2×10^{-6} M

76. 0.02 M monobasic acid dissociates 2%. Hence, pH of the solution is

(*a*) 0.3979 (*b*) 1.3979

(*c*) 1.699 (*d*) 3.3979

77. The pH of 0.1 M acetic acid is 3, the dissociation constant of acid will be

(*a*) 1.0×10^{-4} (*b*) 1.0×10^{-5}

(*c*) 1.0×10^{-3} (*d*) 1.0×10^{-8}

78. The pH value of decinormal solution of NH_4OH which is 20% ionised, is

(*a*) 13.30 (*b*) 14.70

(*c*) 12.30 (*d*) 12.95

SALT HYDROLYSIS, pH CALCULATION: SOLUTIONS OF SALT OF MONOPROTIC ACID AND MONOACIDIC BASE, COMMON ION EFFECT

79. Which is the correct alternate for hydrolysis constant of NH_4CN?

(*a*) $\sqrt{\frac{K_w}{K_a}}$ (*b*) $\frac{K_w}{K_a \times K_b}$

(*c*) $\sqrt{\frac{K_h}{c}}$ (*d*) $\frac{K_a}{K_b}$

80. An aqueous solution of CH_3COONa will be

(*a*) Acidic (*b*) Alkaline

(*c*) Neutral (*d*) None of these

Credit:--- Divansh.....

81. In which of the following salt hydrolysis takes place?

(a) KCl (b) $NaNO_3$

(c) CH_3COOK (d) K_2SO_4

82. When 10 ml of 0.1 M acetic acid ($pK_a = 5.0$) is titrated against 10 ml of 0.1M ammonia solution ($pK_b = 5.0$), the equivalence point occurs at pH

(a) 5.0 (b) 6.0

(c) 7.0 (d) 9.0

83. A solution of $MgCl_2$ in water has pH

(a) < 7 (b) > 7

(c) 7 (d) 14.2

BUFFER SOLUTION

84. The pH of a simple sodium acetate buffer is given by

$$pH = pK_a + \log\frac{[Salt]}{[Acid]};\ K_a \text{ of acetic acid} = 1.8 \times 10^{-5}$$

If [Salt] = [Acid] = 0.1 M, the pH of the solution would be about

(a) 7 (b) 4.7

(c) 5.3 (d) 1.4

85. Which of the following solutions can act as buffer?

(a) 0.1 molar aq. NaCl

(b) 0.1 molar aq. CH_3COOH + 0.1 molar NaOH

(c) 0.1 molar aq. ammonium acetate

(d) None of the above

86. Which of the following solutions cannot act as a buffer?

(a) $NaH_2PO_4 + H_3PO_4$ (b) $CH_3COOH + CH_3COONa$

(c) $HCl + NH_4Cl$ (d) $H_3PO_4 + Na_2HPO_4$

87. One weak acid (like CH_3COOH) and its salt with strong base (like CH_3COONa) is a buffer solution. In which pair this type of characteristic is found?

(a) HCl and NaCl (b) NaOH and $NaNO_3$

(c) KOH and KCl (d) NH_4OH and NH_4Cl

88. 50 ml of 2N acetic acid ($K_a = 1.8 \times 10^{-5}$) is mixed with 10 ml of 1N sodium acetate. The solution will have an approximate pH of

(a) 4 (b) 5 (c) 6 (d) 7

SOLUBILITY AND TITRATION

89. The solubility product of $BaSO_4$ at 25°C is 1.0×10^{-9}. What would be the concentration of H_2SO_4 necessary to precipitate $BaSO_4$ from a solution of 0.01 M Ba^{2+} ions?

(a) 10^{-9} (b) 10^{-8} (c) 10^{-7} (d) 10^{-6}

90. The solubility of $Ca_3(PO_4)_2$ is 's' moles/litre. Then, its solubility product is ______

(a) s^2 (b) $108\ s^5$ (c) $3s^2$ (d) $4\ s^3$

91. The solubility of CaF_2 is 2×10^{-4}. Its solubility product is ______

(a) 2.0×10^{-4} (b) 4.0×10^{-3}

(c) 8.0×10^{-12} (d) 3.2×10^{-11}

Prabal (JEE Main Level)

1. The reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ is studied in a one litre vessel at 250°C. The initial concentration of A was 3n and that of B was n. When equilibrium was attained. equilibrium concentration of C was found to be equal to the equilibrium concentration of B. What is the concentration of D at equilibrium?

(a) n/2 (b) (3n − 1/2)

(c) (n − n/3) (d) n

2. A 20.0 litre vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI, if $K_{eq} = 49$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

(a) 0.78 M (b) 0.039 M

(c) 0.033 M (d) 0.021 M

3. In a chemical equilibrium, the equilibrium constant is found to be 2.5. If the rate constant of backward reaction is 3.2×10^{-2}, the rate constant of forward reaction is -

(a) 8.0×10^{-2} (b) 4.0×10^{-2}

(c) 3.5×10^{-2} (d) 7.6×10^{-3}

4. When alcohol [C_2H_5OH (*l*)] and acetic acid [CH_3COOH (*l*)] are mixed together in equimolar proportion at 27°C, 33% of each is converted into ester. Then, the K_C for the equilibrium

$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ is:

(a) 4 (b) 1/4

(c) 9 (d) 1/9

5. For the reaction equilibrium:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$; the concentration of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol/L respectively. The value of K_c for the reaction is :

(a) 3×10^{-3} M (b) 3×10^{3} M

(c) 3.3×10^{2} M (d) 3×10^{-1} M

6. The equilibrium constant for the reaction:

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction,

$NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is:

(a) 0.02 (b) 50

(c) 4×10^{-4} (d) 2.5×10^{-2}

7. Consider following reactions in equilibrium with equilibrium concentration 0.01 M of every species

(I) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(II) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(III) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Extent of the reactions taking place is:

(a) I > II > III (b) I < II < III

(c) II < III < I (d) III < I < II

8. The equilibrium constant for the reaction $A(g) + 2B(g) \rightleftharpoons C(g)$ is 0.25 $dm^6\ mol^{-2}$. In a volume of 5 dm^3, what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.

(a) 3 moles (b) 24 moles

(c) 26 moles (d) None of these

9. 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The equilibrium constant K_p for dissociation of NH_3 is:

(a) $\frac{1}{0.5} \times (1.5)^3\ atm^{-2}$ (b) $0.5 \times (1.5)^3\ atm^2$

(c) $\frac{0.5 \times (1.5)^3}{3 \times 3}\ atm^2$ (d) $\frac{3 \times 3}{0.5 \times (1.5)^3}\ atm^{-2}$

10. The value of K_p for the reaction, $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$ is 0.03 atm at 427°C, when the partial pressure are expressed in atmosphere, then the value of K_c for the same reaction is

(a) 5.23×10^{-4} (b) 7.34×10^{-4}

(c) 3.2×10^{-3} (d) 5.43×10^{-5}

11. $\log\frac{K_p}{K_c} + \log RT = 0$ is a relationship for the reaction:

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

12. For the following gaseous equilibrium

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ K_p is found to be equal to K_c. This is attained when temperature is

(a) 0°C (b) 273 K

(c) 1 K (d) 12.19 K

13. For the reaction:

$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$. K_p/K_c is:

(a) RT (b) $(RT)^{-1}$

(c) $(RT)^{-1/2}$ (d) $(RT)^{1/2}$

14. At 675 K, $H_2(g)$ and $CO_2(g)$ react to form CO(g) and $H_2O(g)$. K_p for the reaction is 0.16. If a mixture of 0.25 mole of $H_2(g)$ and 0.25 mol of CO_2 is heated at 675 K, mole% of CO(g) in the equilibrium mixture is:

(a) 7.14 (b) 14.28

(c) 28.57 (d) 33.33

15. The value of K_p for the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 50. What is the value of K_c?

(a) 30 (b) 40 (c) 50 (d) 70

16. PCl_5 dissociation in a closed container is shown as:

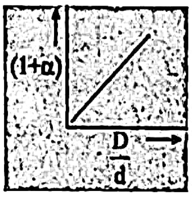
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

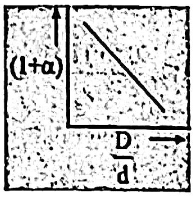
If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is α, the partial pressure of PCl_3 will be:

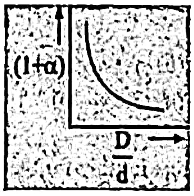
(*a*) $P.\left[\frac{\alpha}{\alpha+1}\right]$ (*b*) $P.\left[\frac{2\alpha}{1-\alpha}\right]$

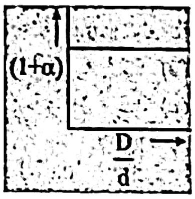
(*c*) $P.\left[\frac{\alpha}{\alpha-1}\right]$ (*d*) $P.\left[\frac{\alpha}{1-\alpha}\right]$

17. In the dissociation of N_2O_4 into NO_2, $(1 + \alpha)$ values with the vapour densities ratio $\left(\frac{D}{d}\right)$ is given by: [α-degree of dissociation, D-vapour density before dissociation, d-vapour density after dissociation]

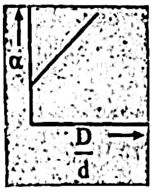
(*a*)


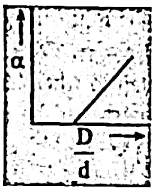
(*b*)


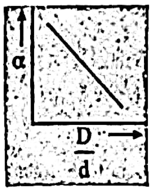
(*c*)


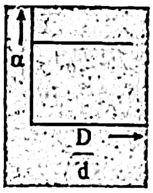
(*d*)


18. In the dissociation of N_2O_4 into NO_2, α varies with the vapour densities ratio $\left(\frac{D}{d}\right)$ is given by: [α-degree of dissociation, D-vapour density before dissociation, d-vapour density after dissociation]

(*a*)


(*b*)


(*c*)


(*d*)


19. For the reaction : $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociation (α) of HI(g) is related to equilibrium constant K_p by the expression:

(*a*) $\frac{1+2\sqrt{K_p}}{2}$ (*b*) $\sqrt{\frac{1+2K_p}{2}}$

(*c*) $\sqrt{\frac{2K_p}{1+2K_p}}$ (*d*) $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

20. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, if percentage dissociation of N_2O_4 are 20%, 45%, 65% & 80%, then the sequence of observed vapour densities will be:

(*a*) $d_{20} > d_{45} > d_{65} > d_{80}$ (*b*) $d_{80} > d_{65} > d_{45} > d_{20}$

(*c*) $d_{20} = d_{45} = d_{65} = d_{80}$ (*d*) $(d_{20} = d_{45}) > (d_{65} = d_{80})$

21. For the reaction,

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$, the degree of dissociation (α) would be –

(*a*) $\frac{\sqrt{K}}{\sqrt{K}+1}$ (*b*) $\sqrt{K}+1$

(*c*) $\sqrt{K}\pm1$ (*d*) $\sqrt{K}-1$

22. An unknown compound A dissociates at 500°C to give products as follows -

$A(g) \rightleftharpoons B(g) + C(g)$

Vapour density of the equilibrium mixture is 40 when it dissociates to the extent of 20%. What will be the molecular weight of Compound A?

(*a*) 96 (*b*) 130 (*c*) 134 (*d*) 140

23. N_2O_4 dissociates as $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 273 K and 2 atm pressure. The equilibrium mixture has a density of 41. What will be the degree of dissociation?

(*a*) 14.2% (*b*) 16.2%

(*c*) 12.2% (*d*) None of these

24. The equation $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for :

(*a*) $A(g) \rightleftharpoons (n/2)B(g) + (n/3)C(g)$

(*b*) $A(g) \rightleftharpoons (n/3)B(g) + (2n/3)C(g)$

(*c*) $A(g) \rightleftharpoons (n/2)B(g) + (n/4)C(g)$

(*d*) $A(g) \rightleftharpoons (n/2)B(g) + C(g)$

25. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$K_c = 66.9$ at 350°C and $K_c = 50.0$ at 448°C. The reaction has

(*a*) $\Delta H = +$ ve

(*b*) $\Delta H = -$ ve

(*c*) $\Delta H =$ zero

(*d*) ΔH sign can not be determined

26. Change in volume of the system does not alter the number of moles in which of the following equilibrium

(*a*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(*b*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(*c*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(*d*) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

27. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by:

(*a*) Adding a suitable catalyst

(*b*) Adding an inert gas

(*c*) Decreasing the volume of container

(*d*) Increasing the amount of CO(g)

28. Given the following reaction at equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected?

(*a*) More $NH_3(g)$ is produced

(*b*) Less $NH_3(g)$ is produced

(*c*) No affect on the equilibrium

(*d*) K_p of the reaction is decreased

29. For an equilibrium $H_2O(s) \rightleftharpoons H_2O(l)$ which of the following statement is true?

(*a*) The pressure changes do not affect the equilibrium.

(*b*) More of ice melts, if pressure on the system is increased.

(*c*) More of liquid freezes, if pressure on the system is increased.

(*d*) The pressure changes may increase or decrease the degree of advancement of the reaction depending upon the temperature of the system.

30. When a bottle of cold drink is opened, the gas comes out with a fizz due to:

(*a*) Decrease in temperature

(*b*) Increase in pressure

(*c*) Decrease in pressure suddenly which results in decrease of solubility of CO_2 gas in water

(*d*) None of these

31. The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct?

(*a*) Concentrations of SO_2, Cl_2 and SO_2Cl_2 do not change

(*b*) More chlorine is formed

(*c*) Concentration of SO_2 is reduced

(*d*) More SO_2Cl_2 is formed

32. The yield of product in the reaction:

$2A(g) + B(g) \rightleftharpoons 2C(g) + Q$ kJ would be lesser at:

(*a*) Low temperature and low pressure

(*b*) High temperature & high pressure

(*c*) Low temperature and high pressure

(*d*) High temperature & low pressure

33. What is the effect of the reduction of the volume of the system for the equilibrium?

$$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$$

(*a*) The equilibrium will be shifted to the left by the increased pressure caused by the reduction in volume.

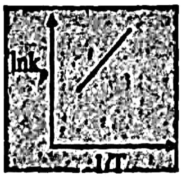
(*b*) The equilibrium will be shifted to the right by the decreased pressure caused by the reduction in volume.

(*c*) The equilibrium will be shifted to the left by the increased pressure caused by the increase in volume.

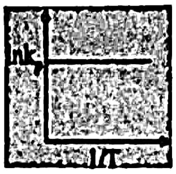
(*d*) The equilibrium will be shifted to the right by the increased pressure caused by the reduction in volume.

34. An exothermic reaction is represented by the graph:

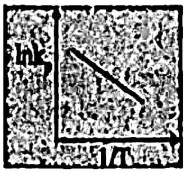
(*a*)



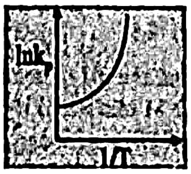
(*b*)



(*c*)



(*d*)



35. Out of the following, amphiprotic species are

I HPO_3^{2-} II $H_2PO_2^-$ III $H_2PO_4^-$ IV HCO_3^-

(*a*) I, III, IV (*b*) I and III

(*c*) III and IV (*d*) All of these

36. Which of the following expression is not true?

(*a*) $[H^+] = [OH^-] = 10^{-7}$ for a neutral solution at 25° C

(*b*) $[H^+] > 10^{-7}$ & $[OH^-] < 10^{-7}$ for an acidic solution at 25° C

(*c*) $[H^+] < 10^{-7}$ & $[OH^-] > 10^{-7}$ for an alkaline solution at 25° C

(*d*) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures.

37. pOH of H_2O is 7.0 at 298 K. If water is heated at 350 K, which of the following statement should be true?

(*a*) pOH will decrease.

(*b*) pOH will increase.

(*c*) pOH will remain 7.0.

(*d*) concentration of H^+ ions will increase but that of OH^- will decrease.

38. One litre of solution contains 10^{-9} moles of OH^- ions at 25°C. Percentage ionisation of water in solution is :

(*a*) 1.8×10^{-7} % (*b*) 1.8×10^{-9} %

(*c*) 3.6×10^{-9} % (*d*) 1.8×10^{-11} %.

39. A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of :

(*a*) 3 (*b*) 4 (*c*) 3000 (*d*) 10,000

40. The $[OH^-]$ in 100.0 ml of 0.016 M-HCl (aq) is:

(*a*) 5×10^{12} M (*b*) 3×10^{-10} M

(*c*) 6.25×10^{-13} M (*d*) 2.0×10^{-9} M.

41. How many moles of NaOH must be removed from one litre of aqueous solution to change its pH from 12 to 11?

(*a*) 0.009 (*b*) 0.01 (*c*) 0.02 (*d*) 0.1

42. Which of the following solutions will have pH close to 1.0?

(*a*) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH

(*b*) 55 ml of (M/10) HCl + 45 ml of (M/10) NaOH

(*c*) 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH

(*d*) 75 ml of (M/5) HCl + 25 ml of (M/5) NaOH.

43. The dissociation constant of acetic acid at a given temperature is 1.69×10^{-5}. The degree of dissociation of 0.01 M acetic acid in the presence of 0.01 M HCl is equal to

(*a*) 0.41 (*b*) 0.13

(*c*) 1.69×10^{-3} (*d*) 0.013

44. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized in:

(*a*) 4.5 (*b*) 2.5 (*c*) 9.5 (*d*) 7.0

45. Find the pH of solution prepared by mixing 25 ml of a 0.5 M solution of HCl, 10ml of a 0.5 M solution of NaOH and 15 ml of water

(*a*) 0.8239 (*b*) 1.0029 (*c*) 1.0239 (*d*) 1.8239

46. Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.

(*a*) 2% (*b*) 4% (*c*) 5% (*d*) 10%

47. Which of the following has the highest degree of ionisation?

(*a*) 1 M NH_3 (*b*) 0.001 M NH_3

(*c*) 0.1 M NH_3 (*d*) 0.0001 M NH_3

48. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is:

(*a*) 1.74×10^{-5} (*b*) 3.52×10^{-3}

(*c*) 6.75×10^{-4} (*d*) 5.38×10^{-2}

49. The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is:

(*a*) 1 (*b*) 2 (*c*) 3 (*d*) 11

50. 1 c.c. of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be

(*a*) 7 (*b*) 3 (*c*) 4 (*d*) 1

51. The degree of hydrolysis of a salt of weak acid and weak base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

(*a*) 100% (*b*) 50%

(*c*) 25% (*d*) None of these

52. What is the percentage hydrolysis of NaCN in $\frac{N}{80}$ solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$?

(*a*) 2.48 (*b*) 5.26 (*c*) 8.2 (*d*) 9.6

53. Which of the following salts undergoes anionic hydrolysis?

(*a*) $CuSO_4$ (*b*) NH_4Cl (*c*) $AlCl_3$ (*d*) K_2CO_3.

54. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

(*a*) 8.58 (*b*) 4.79 (*c*) 7.01 (*d*) 9.22

55. The pH of 0.1 M solution of the following salts increases in the order:

(*a*) $NaCl < NH_4Cl < NaCN < HCl$

(*b*) $HCl < NH_4Cl < NaCl < NaCN$

(*c*) $NaCN < NH_4Cl < NaCl < HCl$

(*d*) $HCl < NaCl < NaCN < NH_4Cl$

56. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is

(*a*) Not a buffer solution and with pH < 7

(*b*) Not a buffer solution with pH > 7

(*c*) A buffer solution with pH < 7

(*d*) A buffer solution with pH > 7

57. If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2 \times 10^{-4}$]. The pOH of the resulting solution is

(*a*) 3.4 (*b*) 3.7 (*c*) 7 (*d*) 10.3

58. The pH of a solution obtained by mixing 100 ml of 0.2 M CH_3COOH with 100 ml of 0.2 M NaOH would be:

(pK_a for $CH_3COOH = 4.74$)

(*a*) 4.74 (*b*) 8.87 (*c*) 9.10 (*d*) 8.57

59. What volume of 0.2 M NH_4Cl solution should be added to 100 ml of 0.1 M NH_4OH solution to produce a buffer solution of pH = 8.7?

Given: pK_b of $NH_4OH = 4.7$; log 2 = 0.3

(*a*) 50 ml (*b*) 100 ml

(*c*) 200 ml (*d*) None of these

60. A solution contains 0.1 M CH_3COOH and 0.1 M CH_3COONa. Which of the following solution will change its pH significantly?

(*a*) Addition of water

(*b*) Addition of small amount of CH_3COONa without change in volume

(*c*) Addition of small amount of CH_3COOH without change in volume

(*d*) None of these

61. K_a for HCN is 5×10^{-10} at 25°C. For maintaining a constant pH of 9, the volume of 5 M KCN solution required to be added to 10 ml of 2 M HCN solution, is (log 2 = 0.3)

(*a*) 4 ml (*b*) 8 ml

(*c*) 2 ml (*d*) 10 ml

62. How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each with respect to weak acid HA and salt $Na^+ A^-$ to make the pH of solution 5.5. Given $pK_a(HA) = 5$ (Use antilog (0.5) = 3.16)

(*a*) 2.08×10^{-1} (*b*) 3.05×10^{-3}

(*c*) 2.01×10^{-2} (*d*) None of these

63. When 100 ml of 0.4 M CH_3COOH are mixed with 100 ml of 0.2 M NaOH, the $[H_3O^+]$ in the solution is approximately: [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$]

(*a*) 1.8×10^{-6} M (*b*) 1.8×10^{-5} M

(*c*) 9×10^{-6} M (*d*) 9×10^{-5} M.

64. If K_{sp} for $HgSO_4$ is 6.4×10^{-5} M^2, then solubility of this substance in mole per m^3 is

(*a*) 8×10^{-3} (*b*) 6.4×10^{-5}

(*c*) 8×10^{-6} (*d*) None of these

65. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed.
(a) 10^{-4} M Ca^{2+} + 10^{-4} M F^-
(b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
(c) 10^{-5} M Ca^{2+} + 10^{-3} M F^-
(d) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

66. The best indicator for the detection of end point in titration of a weak acid and a strong base, is:
(a) Methyl orange (3 to 4)
(b) Methyl red (5 to 6)
(c) Bromothymol blue (6 to 7.5)
(d) Phenolphthalein (8 to 9.6)

67. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:
(a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

68. 50 litre of a solution containing 10^{-5} mole of Ag^+ is mixed with 50 litre of a 2×10^{-7} M HBr solution. $[Ag^+]$ in resultant solution is: [Given: Ksp (AgBr) = 5×10^{-13}]
(a) 10^{-5} M (b) 10^{-6} M
(c) 10^{-7} M (d) None of these

69. What fraction of an indicator HIn is in basic form at a pH of 6, if the pK_a of the indicator is 5?
(a) $\frac{1}{2}$ (b) $\frac{1}{11}$ (c) $\frac{10}{11}$ (d) $\frac{1}{10}$

70. Solubility of MX_4 is 'S' mol/litre, then solubility of MX_4 is related to K_{sp} by:
(a) $S = [K_{sp}/256]^{1/5}$ (b) $S = [128\ K_{sp}]^{1/4}$
(c) $S = [256\ K_{sp}]^{1/5}$ (d) $S = [K_{sp}/128]^{1/4}$

71. If the solubility of lithium sodium hexafluorido aluminate, $Li_3Na_3(AlF_6)_2$ is 's' mol lt^{-1}, its solubility product is equal to:
(a) 729 s^8 (b) 12 s^8
(c) 3900 s^8 (d) 2916 s^8

72. The solubility of CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$) in 0.1 M solution of NaF would be
(a) 3.4×10^{-12} M (b) 3.4×10^{-10} M
(c) 3.4×10^{-9} M (d) 3.4×10^{-13} M

73. In a saturated solution of Ag_2CO_3, silver ion concentration is 2×10^{-4} M. Its solubility product is
(a) 4×10^{-12} (b) 3.2×10^{-11}
(c) 8×10^{-12} (d) 10^{-12}

74. Let the solubilities of AgCl in pure water, 0.01 M $CaCl_2$, 0.01 M NaCl & 0.05 M $AgNO_3$ be s_1, s_2, s_3 & s_4 respectively. What is the correct order of these quantities? Neglect any complexation.
(a) $s_1 > s_2 > s_3 > s_4$ (b) $s_1 > s_2 = s_3 > s_4$
(c) $s_1 > s_3 > s_2 > s_4$ (d) $s_4 > s_2 > s_3 > s_1$

75. The solubility product of $BaCrO_4$ is 2.4×10^{-10} M^2. The maximum concentration of $Ba(NO_3)_2$ possible without precipitation in a 6×10^{-4} M K_2CrO_4 solution, is
(a) 4×10^{-7} M (b) 1.2×10^{10} M
(c) 6×10^{-4} M (d) 3×10^{-4} M.

76. What is the solubility of $Al(OH)_3$, ($K_{sp} = 1 \times 10^{-33}$) in a buffer solution pH = 4?
(a) 10^{-3} M (b) 10^{-4} M
(c) 10^{-4} M (d) 10^{-13} M

77. The solubility of $Fe(OH)_3$ would be maximum in
(a) 0.1 M NaOH (b) 0.1 M HCl
(c) 0.1 M KOH (d) 0.1 M H_2SO_4

78. Arrange in increasing order of solubility of AgBr in the given solutions.
(i) 0.1 M NH_3 (ii) 0.1 M $AgNO_3$
(iii) 0.2 M NaBr (iv) pure water
(a) (iii) < (ii) < (iv) < (i) (b) (iii) < (ii) < (i) < (iv)
(c) (iii) < (ii) = (i) < (iv) (d) (ii) < (iii) < (iv) < (i)

INTEGER TYPE QUESTIONS

79. The equilibrium constant of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 64. If the volume of the container is reduced to one fourth of its original volume, find the value of the equilibrium constant.

80. A mixture of 3 moles of SO_2, 4 moles of NO_2, 1 mole of SO_3 and 4 moles of NO is placed in a 2.0L vessel.
$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$.
At equilibrium, the vessel is found to contain 1 mole of SO_2. Calculate the value of K_c.

81. At elevated temperature, PCl_5 dissociates as,
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
At 300°C, K_p = 11.8 and
$[PCl_3] = [Cl_2] = 0.01$ mol L^{-1} at equilibrium.
$[PCl_5] = x \times 10^{-4}$ mol L^{-1}. What is the value of x?

82. For the following equilibrium starting with 2 moles SO_2 and 1 mole O_2 in 1 L flask,
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
Equilibrium mixture required 0.4 mole MnO_4^- in acidic medium. Hence, value of K_c is______.

83. Calculate the percentage of hydrolysis in a 0.0100 M solution of KCN.(K_a of HCN = 6.2×10^{-10})

84. Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to 100 times.
[Given: K_a of $CH_3CO_2H = 10^{-5}$ M]

85. Dissociation constant for a weak base BOH is 10^{-5}. Calculate the value of pH when it is half neutralized by HCl?

Credit:--- Divansh.....

86. 0.15 mole of pyridinium chloride has been added into 500 cm^3 of 0.2 M pyridine solution. Calculate pH in the resulting solution assuming no change in volume. (K_b for pyridine = 1.5×10^{-9} M)

87. What volume (in ml) of 0.10 M sodium formate solution should be added to 50 ml of 0.05 M formic acid to produce a buffer solution of pH 4. [pK_a for formic acid is 3.7]

88. How much water (in L) should be added to 10 g CH_3COOH to give pOH equal to 11. K_a (CH_3COOH) = 1.8×10^{-5}

89. 10 ml of 0.1 M weak acid HA ($K_a = 10^{-5}$) is mixed with 10 ml 0.2 M HCl and 10 ml 0.1 M NaOH. Find the concentration of A^- in the resulting solution. Write your answer as ($-\log[A^-]$).

Parikshit (JEE Advanced Level)

SINGLE CORRECT TYPE QUESTIONS

1. The solubility of Ag_2CO_3 in water at 25°C is 1×10^{-4} mole/litre. What is its solubility in 0.01 M Na_2CO_3 solution? Assume no hydrolysis of CO_3^{2-} ion.
   (a) 6×10^{-6} mole/litre
   (b) 4×10^{-5} mole/litre
   (c) 10^{-5} mole /litre
   (d) 2×10^{-5} mole/litre

2. An industrial fuel, 'water gas', which consists of a mixture of H_2 and CO can be made by passing steam over red-hot carbon. The reaction is
   $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$, $\Delta H = +131$ kJ/mol
   The yield of CO and H_2 at equilibrium would be increased by:
   (a) Raising the total pressure of the steam
   (b) Adding hot carbon
   (c) Raising the temperature
   (d) Reducing the volume of the system

3. A solution contains HCl, $Cl_2HCCOOH$ & CH_3COOH at concentation 0.09 M in HCl, 0.09 M in $Cl_2HCCOOH$ & 0.1 M in CH_3COOH. pH for the solution is 1. Ionization constant of $CH_3COOH = 10^{-5}$. What is the magnitude of K_a for dichloroacetic acid?
   (a) $K_a = 1.25\times10^{-2}$ (b) $K_a = 2.25\times10^{-2}$
   (c) $K_a = 3.75\times10^{-4}$ (d) $K_a = 5.75\times10^{-2}$

4. In the reaction $X(g) + Y(g) \rightleftharpoons 2Z(g)$, 2 mole of X, 1 mole of Y and 1 mole of Z are placed in a 10 litre vessel and allowed to reach equilibrium. If final concentration of Z is 0.2 M, then K_c for the given reaction is:
   (a) 1.60 (b) $\frac{80}{3}$
   (c) $\frac{16}{3}$ (d) None of these

5. $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$. We started with 1 mole of I_2 and 0.5 mole of I^- in one litre flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mole of yellow precipitate. Equilibrium constant K_c is:
   (a) 1.33 (b) 2.66
   (c) 2.0 (d) 3.0

6. For the reaction $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$; K_p is 5×10^{-2} atm. Calculate the mole per cent of $C_2H_6(g)$ at equilibrium if pure C_2H_6 at 1 atm is passed over a suitable catalyst at 900 K:
   (a) 20 (b) 33.33
   (c) 66.66 (d) None of these

7. At a certain temperature and 2 atm pressure equilibrium constant (K_p) is 25 for the reaction
   $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
   Initially if we take 2 moles of each of the four gases and 2 moles of inert gas, what would be the equilibrium partial pressure of NO_2?
   (a) 1.33 atm
   (b) 0.1665 atm
   (c) 0.133 atm
   (d) None of these

8. When N_2O_5 is heated at certain temperature, it dissociates as $N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g)$; $K_c = 2.5$. At the same time N_2O_3 also decomposes as: $N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g)$. If initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to dissociate. Concentration of O_2 at equilibrium is 2.5 M. Equilibrium concentration of N_2O_5 is:
   (a) 1.0 M (b) 1.5 M
   (c) 2.166 M (d) 1.846 M

9. Two solid compounds X and Y dissociates at a certain temperature as follows
   $X(s) \rightleftharpoons A(g) + 2B(g)$; $K_{p_1} = 9\times10^{-3}$ atm^3
   $Y(s) \rightleftharpoons 2B(g) + C(g)$; $K_{p_2} = 4.5\times10^{-3}$ atm^3
   The total pressure of gases over a mixture of X and Y is:
   (a) 4.5 atm (b) 0.45 atm
   (c) 0.6 atm (d) None of these

10. Ammonium carbamate dissociates as,
    $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
    In a closed vessel containing ammonium carbamate in equilibrium with its vapour, ammonia is added such that partial pressure of NH_3 now equals the original total pressure. Thus, ratio of the total pressure to the original pressure is
    (a) 2:1 (b) 31:27
    (c) 27:37 (d) $\sqrt{27}:\sqrt{31}$

Credit:--- Divansh.....

11. For the given endothermic equilibrium, the heat of reaction at constant volume is 1200 cal more than that of heat of reaction at constant pressure at 300 K. The ratio of equilibrium constants K_P and K_C for the above equilibrium is:

(*a*) 3.6×10^5 (*b*) 6.2×10^6

(*c*) 3.6×10^{-5} (*d*) 1.64×10^{-3}

12. Calculate the ratio of $[HCOO^-]$ and $[F^-]$ in a mixture of 0.2 M HCOOH ($K_a = 2 \times 10^{-4}$) and 0.1 M HF ($K_a = 6.6 \times 10^{-4}$)

(*a*) 1 : 6.6 (*b*) 1 : 3.3

(*c*) 2 : 3.3 (*d*) 3.3 : 2

13. The simultaneous solubility of AgCN ($K_{sp} = 2.5 \times 10^{-16}$) and AgCl ($K_{sp} = 1.6 \times 10^{-10}$) in 1.0 M NH_3(aq.) are respectively : [Given : $K_f\,[Ag(NH_3)_2^+] = 10^7$]

(*a*) $0.037, 5.78 \times 10^{-8}$ (*b*) $5.78 \times 10^{-8}, 0.037$

(*c*) $0.04, 6.25 \times 10^{-8}$ (*d*) $1.58 \times 10^{-3}, 1.26 \times 10^{-5}$

14. Two moles of an equimolar mixture of two alcohols. R_1-OH and R_2-OH are esterified with one mole of acetic acid. If 80% of the acid is consumed and the quantities of ester formed under equilibrium are in the ratio of 3:2, the value of the equilibrium constant for the esterification of R_1-OH with acetic acid is

(*a*) 3.69 (*b*) 3.12

(*c*) 1.34 (*d*) 3.51

15. P_3Q_2 is a sparingly soluble salt of molar mass M ($g.mol^{-1}$) and solubility x $g.lit^{-1}$. The ratio of the molar concentration of Q^{3-} to the solubility product of the salt is

(*a*) $\frac{1}{54}\frac{M^4}{x^4}$ (*b*) $\frac{M^3}{27x^3}$

(*c*) $\frac{M^3}{27^{1/2}x^{3/2}}$ (*d*) $54\frac{x^5}{M^5}$

16. In the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + Heat. One mole of N_2 reacts with three moles of H_2. If at equilibrium 'x' moles of N_2 are combined, then the value of 'x' in terms of K_p and the total pressure of gases at equilibrium P is ($x << 1$)

(*a*) $\frac{3P.\sqrt{3.K_P}}{8}$ (*b*) $\frac{8P}{3\sqrt{3.K_P}}$

(*c*) $\frac{3\sqrt{3.K_P}}{8P}$ (*d*) $\frac{8}{P}\sqrt{\frac{K_P}{3}}$

MULTIPLE CORRECT TYPE QUESTIONS

17. The two equilibria, $AB \rightleftharpoons A^+ + B^-$ and $AB + B^- \rightleftharpoons AB_2^-$ are simultaneously maintained in a solution with equilibrium constants, K_1 and K_2 respectively. If $[A^+]$ and $[AB_2^-]$ are y and x respectively, under equilibrium produced by adding the substance AB(s) to the solvent then :

(*a*) $(K_1/K_2) = \frac{y}{x}(y - x)^2$ (*b*) $(K_1/K_2) = \frac{y}{x}(x - y)$

(*c*) $[B^-]_{eq.} = y - x$ (*d*) None of these

18. (*i*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g); K_1$

(*ii*) $\left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g) \rightleftharpoons NO(g); K_2$

(*iii*) $2NO(g) \rightleftharpoons N_2(g) + O_2(g); K_3$

(*iv*) $NO(g) \rightleftharpoons \left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g); K_4$

Correct relation between K_1, K_2, K_3 and K_4 is/are:

(*a*) $K_1 \times K_3 = 1$ (*b*) $\sqrt{K_1} \times K_4 = 1$

(*c*) $\sqrt{K_3} \times K_2 = 1$ (*d*) None of these

19. Consider the equilibrium $HgO(s) + 4I^-(aq) + H_2O(l) \rightleftharpoons HgI_4^{2-}(aq) + 2OH^-(aq)$, which changes will decrease the equilibrium concentration of HgI_4^{2-}?

(*a*) Addition of 0.1 M HI (aq)

(*b*) Addition of HgO(s)

(*c*) Addition of H_2O (*l*)

(*d*) Addition of KOH (aq)

20. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperature is favoured by

(*a*) Introducing an inert gas at constant volume

(*b*) Introducing chlorine gas at constant volume

(*c*) Introducing an inert gas at constant pressure

(*d*) Introducing PCl_5 at constant volume.

21. The reactions

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ and $COCl_2(g) \rightleftharpoons CO(g) + Cl_2$ (g) are simultaneously in equilibrium in an equilibrium box at constant volume. A few moles of CO(g) are later introduced into the vessel. After some time, the new equilibrium concentration of

(*a*) PCl_5 will remain unchanged

(*b*) Cl_2 will be greater

(*c*) PCl_5 will become less

(*d*) PCl_3 will become greater

22. Which of the following statements are correct at 25°C?

(*a*) pK_a for H_3O^+ is 15.74

(*b*) pK_b for OH^- is –1.74

(*c*) $pK_a + pK_b = pK_w$ for HCl & HOCl

(*d*) percentage dissociation of water is 1.8×10^{-7} %

23. Which of following solution can act as buffer?

(*a*) NaCl + NaOH (*b*) Borax + Boric acid

(*c*) $NaH_2PO_4 + Na_2HPO_4$ (*d*) $NH_4Cl + NH_4OH$

24. Equal volumes of following solutions are mixed. In which case the pH of resulting solution will be average value of pH of two solutions?

(*a*) Aqueous HCl of pH = 2, aqueous NaOH of pH = 12

(*b*) aqueous HCl of pH = 2, aqueous HCl of pH = 4

(*c*) Aqueous NaOH of pH = 12, aqueous NaOH of pH = 10

(*d*) Aqueous CH_3COOH of pH = 5, aqueous NH_3 of pH = 9. [$K_a(CH_3COOH) = K_b(NH_3)$]

Credit:--- Divansh.....

25. Which of the following solutions when added to 1 L of a 0.01 M CH_3COOH solution will cause no change in the degree of dissociation of CH_3COOH and pH of the solution? $K_a = 1.6 \times 10^{-5}$ for CH_3COOH

(*a*) 0.6 mM HCOOH ($K_a = 8 \times 10^{-4}$)

(*b*) 0.1 M CH_3COONa

(*c*) 0.4 mM HCl

(*d*) 0.01 M CH_3COOH

26. 100 ml of 0.5 M hydrazoic acid (HN_3, $K_a = 3.6 \times 10^{-4}$) and 400 ml of 0.1 M cyanic acid (HOCN, $K_a = 8 \times 10^{-4}$) are mixed. which of the following is (are) true for the final solution?

(*a*) $[H^+] = 10^{-2}$ M (*b*) $[N_3^-] = 3.6 \times 10^{-3}$ M

(*c*) $[OCN^-] = 6.4 \times 10^{-3}$ M (*d*) $[H^+] = 1.4 \times 10^{-2}$ M

27. K_a values for HA, HB and HD are 10^{-5}, 10^{-7} and 10^{-9} respectively. Which of the following will be correct for decimolar aqueous solutions of NaA, NaB and NaD at 25°C?

(*a*) $(pH)_{NaA} < (pH)_{NaB}$ (*b*) $(pH)_{NaD} < (pH)_{NaB}$

(*c*) $(pH)_{NaA} < (pH)_{NaD}$ (*d*) $(pH)_{NaB} = 7$

28. 0.1 M CH_3COOH is diluted at 25°C ($K_a = 1.8 \times 10^{-5}$), then which of the following is found to be correct?

(*a*) $[H^+]$ will increase

(*b*) pH will increase

(*c*) Number of H^+ will increase

(*d*) All the above are correct

29. When 0.1 mol arsenic acid (H_3AsO_4) is dissolved in 1L buffer solution of pH = 8, which of the following hold good? For arsenic acid: $K_1 = 2.5 \times 10^{-4}$, $K_2 = 5 \times 10^{-8}$, $K_3 = 2 \times 10^{-13}$. ['<<' sign denotes that the high concentration is at least 100 times more than the lower one]

(*a*) $[H_3AsO_4] << [H_2AsO_4^-]$

(*b*) $[H_2AsO_4^-] << [HAsO_4^{2-}]$

(*c*) $[HAsO_4^{2-}] << [H_2AsO_4^-]$

(*d*) $[AsO_4^{3-}] << [HAsO_4^{2-}]$

30. Which of the following mixtures will act as buffer?

(*a*) H_2CO_3 + NaOH (1.5:1 molar ratio)

(*b*) H_2CO_3 + NaOH (1.5:2 molar ratio)

(*c*) NH_4OH + HCl (5 : 4 molar ratio)

(*d*) NH_4OH + HCl (4 : 5 molar ratio)

31. Let the colour of the indicator HIn (colourless) will be visible only when its ionised form (pink) is 25% or more in a solution. Suppose HIn ($pK_a = 9.0$) is added to a solution of pH = 9.6, then predict what will happen? (Take log 2 = 0.3)

(*a*) Pink colour will be visible

(*b*) Pink colour will not be visible

(*c*) % of ionised form will be less than 25%

(*d*) % of ionised form will be more than 25%

32. A 2.5 gm impure sample containing weak monoacidic base (Mol. wt. = 45) is dissolved in 100 ml water and titrated with 0.5 M HCl when $\left(\frac{1}{5}\right)^{th}$ of the base was neutralised, the pH was found to be 9 and at equivalence point, pH of solution is 4.5. Given: All data are at 25°C & log 2 = 0.3. Select correct statement(s).

(*a*) K_b of weak monoacidic base is less than 10^{-6}.

(*b*) Concentration of salt (c) at equivalence point is 0.25 M.

(*c*) Volume of HCl used at equivalence point is 100 ml.

(*d*) Weight percentage of base in given sample is 80%.

33. In which of the following solutions, the solubility of AgCN will be greater than that in pure water?

Given: $K_{sp}(AgCN) = 4 \times 10^{-16}$, K_a (HCN) $= 5 \times 10^{-10}$

(*a*) 0.01 M $AgNO_3$ solution

(*b*) A buffer solution of pH = 12

(*c*) 0.2 M NH_3 solution

(*d*) A buffer solution of pH = 5

34. The solubility of a sparingly soluble salt A_xB_y in water at 25°C = 1.4×10^{-4} M. The solubility product is 1.1×10^{-11}. The possibilities are

(*a*) x = 1, y = 2 (*b*) x = 2, y = 1

(*c*) x = 1, y = 3 (*d*) x = 3, y = 1

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 35 to 37): 4.4 grams of CO_2 are introduced into a 0.82 L flask containing excess solid carbon at 627°C, so that the equilibrium

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

is reached. The density of equilibrium gaseous mixture corresponds to an average molecular weight of 36.

[R = 0.082 L atm $mol^{-1}K^{-1}$; C = 12, O = 16]

35. Total number of moles of equilibrium gaseous mixture is

(*a*) $\frac{1}{30}$ (*b*) $\frac{2}{15}$

(*c*) $\frac{1}{15}$ (*d*) $\frac{1}{10}$

36. K_P of the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, is

(*a*) 6 atm (*b*) 12 atm

(*c*) 24 atm (*d*) 15 atm

37. If in the above problem actually 1.2 g of solid carbon is present initially, how many total moles of CO_2 would have to be introduced initially so that at equilibrium only a trace of carbon remained?

(*a*) 0.25 (*b*) 0.7

(*c*) 0.6 (*d*) 0.4

Credit:--- Divansh.....

Comprehension (Q. 38 to 40): Strontium fluoride (SrF_2) is a sparingly soluble salt. Let s_1 be its solubility (in mol/L) in pure water at 25°C, assuming no hydrolysis of F^- ions. Also, let s_2 be its solubility (in mol/L) in 0.1 M NaF solution at 25°C, assuming no hydrolysis of F^- ions and no complex formation.

However, it is known that $s_1 : s_2 = 10^6 : 256$. Now, answer the following questions:

38. The K_{sp} value of SrF_2 at 25°C is:
    (a) 2.048×10^{-9} (b) 1.372×10^{-9}
    (c) 1.864×10^{-9} (d) 2.916×10^{-9}

39. The mass of NaF to be added to 100 ml solution of 0.0011 M Sr^{+2} ions to reduce its concentration to 2×10^{-4} M is: [Assume no hydrolysis of F^- ions]
    (a) 0.42 g (b) 0.063 g
    (c) 0.021 g (d) 0.084 g

40. The solubility of SrF_2 (in mol/L) in a buffer solution of pH = 5 at 25°C is: [Given: K_a for HF = $\frac{1}{7} \times 10^{-5}$]
    (a) 1.6×10^{-3} (b) 3.2×10^{-3}
    (c) 4.8×10^{-3} (d) 6.4×10^{-3}

MATCH THE COLUMN TYPE QUESTIONS

41. Match the following

	Column-I		Column-II
A.	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (T = 300°C)	p.	$\Delta n_g > 0$
B.	$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (T = 50°C)	q.	$K_p < K_c$
C.	$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	r.	K_p not defined
D.	$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$	s.	$P_{initial} > P_{eqb.}$

(a) A-(s); B-(p); C-(q); D-(r)
(b) A-(q,s); B-(p); C-(p); D-(r)
(c) A-(q,s); B-(p,q); C-(p); D-(r)
(d) A-(q,s); B-(p); C-(p,q); D-(r)

42. Match the following:

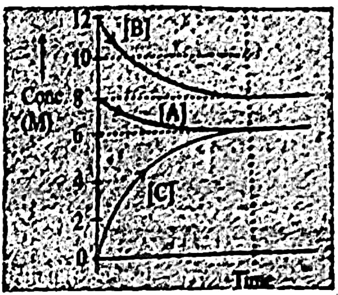
	Column-I		Column-II (factors affecting forward direction)
A.	$A_2(g) + B_2(g) \xrightleftharpoons{\text{Endothermic}} 2AB(g)$	p.	High temperature
B.	$2AB_2(g) + B_2(g) \xrightleftharpoons{\text{Exothermic}} AB_3(g)$	q.	Low temperature
C.	$2AB_3(g) + A_2(g) \xrightleftharpoons{\text{Exothermic}} 2A_2(g) + 3B_2(g)$	r.	High pressure
		s.	Low pressure
		t.	Independent of pressure

(a) A-(q,t); B-(q,r); C-(q,s)
(b) A-(p,r); B-(q,t); C-(q,s)
(c) A-(p,t); B-(q,r); C-(q,s)
(d) A-(p,t); B-(q,s); C-(q,t)

INTEGER TYPE QUESTIONS

43. An unknown compound A dissociates at 500°C to give products as follows -
    $A(g) \rightleftharpoons B(g) + C(g) + D(g)$
    Vapour density of the equilibrium mixture is 50 when it dissociates to the extent to 10%. What will be the molar mass (in g/mol) of compound A?

44. The gaseous reaction : $A(g) + nB(g) \rightleftharpoons mC(g)$ is represented by following curves



What is the value of (n + m)?

45. A standard solution of I_2 in water contains 0.33 g of I_2 in one litre flask. More than this dissolves in a KI solution because of the following equilibrium: $I_2 + I^- \rightleftharpoons I_3^-$. A 0.1 M KI solution actually dissolves 12.5 g of iodine per litre, most of which is converted to I_3^-. Assuming that concentration of I_2 in all saturated solution is the same, calculate the equilibrium constant for the above reaction.

46. A solution of weak acid HA was titrated with base NaOH. The equivalent point was reached when 40 mL of 0.1 M NaOH has been added. Now 20 mL of 0.1 M HCl were added to titrated solution, the pH was found to be 5.0. What will be the pH of the solution obtained by mixing 20 mL of 0.2 M NaOH and 20 mL of 0.2 M HA?

47. A solution is saturated in $SrCO_3$ and SrF_2. The CO_3^{2-} was found to be 10^{-3} mol/L. If the concentration of F^- in solution is represented as $y \times 10^{-2}$ M then what is the value of y? [Given: $K_{sp}(SrCO_3) = 2.5 \times 10^{-10}$; $K_{sp}(SrF_2) = 10^{-10}$].

48. Equal volume of 0.1 M H_2CO_3 ($K_{a_1} = 10^{-7}$; $K_{a_2} = 10^{-11}$) and 0.1 M H_2S ($K_{a_1} = 10^{-7}$, $K_{a_2} = 10^{-14}$) are mixed together. Calculate value of (pOH – pH) for resulting solution?

49. 200 mL of 0.2 M H_2SO_4 is diluted to 900 ml by adding water. Solution is then reacted with 100 mL, 0.6 M NaOH solution. The resulting sample is further reacted with 100 mL of 0.2 M $Ca(OH)_2$ solution and then 100 mL H_2O was vaporised. Calculate final pH and write the value of pH × 10.

50. When NaOH solution is gradually added to the solution of a weak acid (HA), the pH of the solution is found to be 5.0 at the addition of 10.0 mL of NaOH and 6.0 at the further addition of 10.0 mL of same NaOH. (Total volume of NaOH = 20 mL) calculate pK_a for HA [log 2 = 0.3]
    [Multiply final answer by 10]

Credit:--- Divansh.....

NUMERICAL TYPE QUESTIONS

51. A buffer solution having 0.04 M in Na_2HPO_4 and 0.02 M in Na_3PO_4 is prepared. The electrolytic oxidation of 1.0 millimole of the organic compound RNHOH is carried out in 100 mL of the buffer. The reaction is

$RNHOH + H_2O \rightarrow RNO_2 + 4H^+ + 4e^-$

The approximate pH of solution after the oxidation is complete is:

[Given : for H_3PO_4, $pK_{a_1} = 2.2$; $pK_{a_2} = 7.20$; $pK_{a_3} = 12$]

(Answer Upto One Decimal Place)

52. Given, $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, $K_{a_1} = 4.3 \times 10^{-7}$

and $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$, $K_{a_2} = 4.8 \times 10^{-11}$

Thus, fraction of carbonate present as H_2CO_3 in the solution of pH 10.00 is $x \times 10^{-4}$. Find x.

(Answer Upto One Decimal Place)

53. 50 ml of a solution which is 0.05 M in the acid HA ($pK_a = 3.80$) and 0.1 M in HB ($pK_a = 8.20$) is titrated with 0.2 M-NaOH solution. Calculate the pH of solution at the first equivalence point. Give your answer after multiplying with 100. **(Answer Upto Two Decimal Place)**

54. H_2SO_4 solution (density = 1.8 gm L^{-1}) is 500 m. Thus, its pH is - x. Find x. **(Answer Upto Two Decimal Place)**

55. Iron filings and water were placed in a 5.0 liter tank and sealed. The tank was heated to 1000°C. Upon analysis the tank was found to contain 1.10 g of di-hydrogen and 42.50 g of water vapour. The following reaction occurred in the tank:

$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

Calculate the equilibrium constant (K_c) for the reaction when conc^{n}s are taken in mol/L.

(Answer Upto four Decimal Place)

PYQ's (Past Year Questions)

EQUILIBRIUM IN PHYSICAL AND CHEMICAL PROCESSES

1. The number of correct statements involving equilibria in physical process from the following is

[10 April, 2023 (Shift-I)]

(*a*) Equilibrium is possible only in a closed system at a given temperature

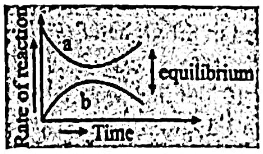
(*b*) Both the opposing processes occur at the same rate.

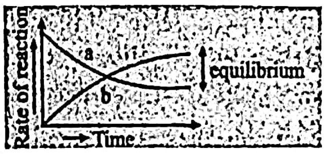
(*c*) When equilibrium is attained at a given temperature, the value of all its parameters became equal

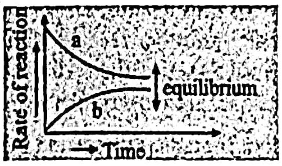
(*d*) For dissolution of solids in liquids, the solubility is constant at a given temperature

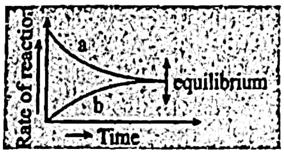
2. For the equilibrium $A \rightleftharpoons B$, the variation of the rate of the forward (a) and reverse (B) reaction with time is given by:

[4 Sept, 2020 (Shift-I)]

(*a*) 

(*b*) 

(*c*) 

(*d*) 

LAW OF CHEMICAL EQUILIBRIUM CONSTANT AND APPLICATIONS OF EQUILIBRIUM CONSTANTS

3. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, K_p = 0.492 atm at 300K. K_c for the reaction at same temperature is___ $\times 10^{-2}$. (Given: R = 0.082 L atm mol^{-1} K^{-1})

[29 Jan, 2024 (Shift-I)]

4. The following concentrations were observed at 500 K for the formation of NH_3 from N_2 and H_2. At equilibrium: $[N_2] = 2 \times 10^{-2}$ M, $[H_2] = 3 \times 10^{-2}$ M and $[NH_3] = 1.5 \times 10^{-2}$ M. Equilibrium constant for the reaction is_______.

[29 Jan, 2024 (Shift-II)]

5. The pH at which $Mg(OH)_2$ [$K_{sp} = 1 \times 10^{-11}$] begins to precipitate from a solution containing 0.10 M Mg^{2+} ions is______ **[30 Jan, 2024 (Shift-I)]**

6. For the given reaction, choose the correct expression of K_C from the following: **[31 Jan, 2024 (Shift-I)]**

$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons (FeSCN)^{2+}_{(aq)}$

(*a*) $K_C = \dfrac{[(FeSCN)^{2+}]}{[Fe^{3+}][SCN^-]}$

(*b*) $K_C = \dfrac{[Fe^{3+}][SCN^-]}{[FeSCN^{2+}]}$

(*c*) $K_C = \dfrac{[FeSCN^{2+}]}{[Fe^{3+}]^2[SCN^-]^2}$

(*d*) $K_C = \dfrac{[FeSCN^{2+}]^2}{[Fe^{3+}][SCN^-]}$

Credit:--- Divansh.....

7. $A_{(g)} \rightleftharpoons B_{(g)} + \frac{\;}{2}{}_{(g)}$ The correct relationship between K_p, α and equilibrium pressure P is **[31 Jan, 2024 (Shift-II)]**

(a) $K_p = \frac{\alpha^{1/2}p^{1/2}}{(2+\alpha)^{1/2}}$ (b) $K_p = \frac{\alpha^{3/2}p^{1/2}}{(2+\alpha)^{1/2}(1-\alpha)}$

(c) $K_p = \frac{\alpha^{1/2}p^{3/2}}{(2+\alpha)^{3/2}}$ (d) $K_p = \frac{\alpha^{1/2}p^{1/2}}{(2+\alpha)^{3/2}}$

8. At –20°C and 1 atm pressure, a cylinder is filled with equal number of H_2, I_2 and HI molecules for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the K_P for the process is $x \times 10^{-1}$. x = ________.

[Given: $R = 0.082$ L atm K^{-1} mol^{-1}]

[06 April, 2024 (Shift-I)]

(a) 2 (b) 1 (c) 10 (d) 0.01

9. The ratio $\frac{K_P}{K_C}$ for the reaction: **[06 April, 2024 (Shift-II)]**

$CO_{(g)} + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ is:

(a) $(RT)^{1/2}$ (b) RT

(c) 1 (d) $\frac{1}{\sqrt{RT}}$

10. For the given hypothetical reactions, the equilibrium constants are as follows:

$X \rightleftharpoons Y; K_1 = 1.0$
$Y \rightleftharpoons Z; K_2 = 2.0$
$Z \rightleftharpoons W; K_3 = 4.0$

The equilibrium constant for the reaction $X \rightleftharpoons W$ is **[08 April, 2024 (Shift-I)]**

(a) 6.0 (b) 12.0 (c) 8.0 (d) 7.0

11. The equilibrium constant for the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

is $K_C = 4.9 \times 10^{-2}$. The value of K_C for the reaction given below is **[04 April, 2024 (Shift-II)]**

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ is}$$

(a) 4.9 (b) 41.6 (c) 49 (d) 416

12. The equilibrium constant for the reaction

$A(s) \rightleftharpoons M(s) + \frac{1}{2}O_2(g)$ **[27 July, 2021 (Shift-II)]**

is $K_p = 4$. At equilibrium, the partial pressure of O_2 is ________ atm.

(Round off to the Nearest Integer).

13. For the following assertion and reason, the correct option is **[2 Sept, 2020 (Shift-I)]**

Assertion (A): When Cu(II) and sulphide ions are mixed they react together extremely quickly to give a solid

Reason (R): The equilibrium constant of Cu^{2+} (aq) + S^{2-}(aq) $\rightleftharpoons$ CuS(s) is high because the solubility product is low.

(a) (A) is false and (R) is true.
(b) Both (A) and (R) are false.
(c) Both (A) and (R) are true but (R) is not the explanation for (A).
(d) Both (A) and (R) are true and (R) is the explanation for (A).

14. In a chemical reaction $A + 2B \overset{K}{\rightleftharpoons} 2C + D$, the initial concentration of B was 1.5 times of A but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is **[12 Jan, 2019 (Shift-I)]**

(a) 4 (b) 16 (c) 1/4 (d) 1

15. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17}.

$Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)$

When equal volumes of 0.06 M Fe^{2+} (aq) and 0.2 M S^{2-} (aq) solutions are mixed, the equilibrium concentration of Fe^{2+} (aq) is found to be $Y \times 10^{-17}$ M. The value of Y is ______ **[JEE Adv 2019]**

RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT (K), REACTION QUOTIENT (Q) AND GIBB'S ENERGY (G)

16. Consider the following reaction at 298 K.

$\frac{3}{2}O_{2(g)} \rightleftharpoons O_{3(g)} \cdot K_P = 2.47 \times 10^{-29}$.

$\Delta_r G^\ominus$ for the reaction is ______ kJ.

(Given $R = 8.314$ JK^{-1} mol^{-1}) **[31 Jan, 2024 (Shift-I)]**

17. (i) $X(g) \rightleftharpoons Y(g) + Z(g)$ $K_{p_1} = 3$ **[1 Feb, 2023 (Shift-I)]**

(ii) $A(g) \rightleftharpoons 2B(g)$ $K_{p_2} = 1$

If the degree of dissociation and initial concentration of both the reactants X(g) and A(g) are equal, then the ratio of the total pressure at equilibrium $\left(\frac{p_1}{p_2}\right)$ is equal to x : 1.

The value of x is ________ (Nearest integer)

18. The gas phase reaction

$2A(g) \rightleftharpoons A_2(g)$

At 400 K, $\Delta G^\circ = +25.2$ kJ mol^{-1}.

The equilibrium constant K_C for this reaction is ______ $\times 10^{-2}$. (Round off to the nearest integer).

[Use : $R = 8.3$ J mol^{-1} K^{-1}, ln10 = 2.3, $\log_{10}2 = 0.30$, 1atm = 1 bar]

[antilog (–0.3) = 0.501] **[18 March, 2021 (Shift-II)]**

Credit:--- Divansh.....

19. The variation of equilibrium constant with temperature is given below: **[15 Sept, 2020 (Shift-I)]**

Temperature	Equilibrium Constant
$T_1 = 25°C$	$K_1 = 10$
$T_2 = 100°C$	$K_2 = 100$

The value of $\Delta H°, \Delta G°$ at T_1 and $\Delta G°$ at T_2 ________ (in kJ mol^{-1}) respectively, are close to

[Use $R = 8.314 JK^{-1}mol^{-1}$]

(*a*) 28.7, –7.14 and –5.71 (*b*) 0.64, –7.14 and –5.71

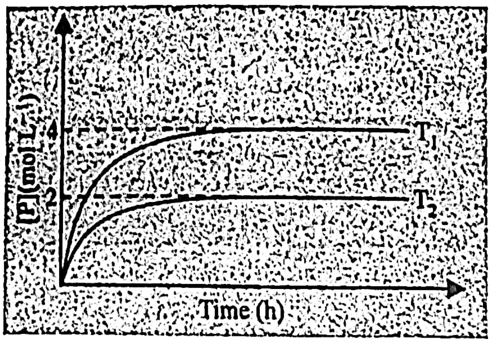
(*c*) 28.4, –5.71 and –14.29 (*d*) 0.64, –5.71 and –14.29

20. The INCORRECT match in the following is: **[12 April, 2019 (Shift-II)]**

(*a*) $\Delta G° < 0, K < 1$ (*b*) $\Delta G° = 0, K = 1$

(*c*) $\Delta G° > 0, K < 1$ (*d*) $\Delta G° < 0, K > 1$

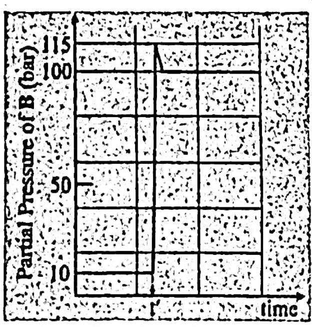
21. In a one-litre flask, 6 moles of A undergoes the reaction A (g) $\rightleftharpoons$ P(g). The progress of product formation at two temperatures (in Kelvin), T_1 and T_2, is shown in the figure: **[JEE Adv 2023]**



If $T_1 = 2T_2$ and $(\Delta G_2^\ominus - \Delta G_1^\ominus) = RT_2 \ln x$, then the value of x is ______.

[$\Delta G_1^\ominus$ and $\Delta G_2^\ominus$ are standard Gibb's free energy change for the reaction at temperatures T_1 and T_2, respectively.]

22. Consider the reaction A $\rightleftharpoons$ B at 1000 K. At time t′, the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment, the partial pressure of A was maintained at 1 bar. Given below is the plot of the partial pressure of B with time. What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K? **[JEE Adv 2020]**



FACTORS AFFECTING EQUILIBRIUM AND ACIDS, BASES & SALTS

23. The following reaction occurs in the Blast furnace where iron ore is reduced to iron metal

$$Fe_2O_{3(s)} + 3CO_{(g)} \rightleftharpoons Fe_{(l)} + 3CO_{2(g)}$$

Using the Le-Chatelier's principle, predict which one of the following will not disturb the equilibrium. **[05 April, 2024 (Shift-I)]**

(*a*) Addition of Fe_2O_3

(*b*) Addition of CO_2

(*c*) Removal of CO

(*d*) Removal of CO_2

24. Which of the following statement(s) is/are correct? **[15 April, 2023 (Shift-I)]**

(A) The pH of 1×10^{-8} solution is 8.

(B) The conjugate base $H_2PO_4^-$ is $H_2PO_4^{2-}$.

(C) K_W increases with increase in temperature.

(D) When a solution of weak monoprotic acid is titrated against a strong base at half neutralisation point, $pH = \frac{1}{2}pK_a$

Choose the correct answer from the option given below.

(*a*) (B), (C), (D) (*b*) (A), (D)

(*c*) (A), (B), (C) (*d*) (B), (C)

25. Consider the following reaction:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $\Delta H^0 = +58$ kJ

For each of the following cases (a, b), the direction in which the equilibrium shifts is: **[5 Sept, 2020 (Shift-I)]**

(*i*) Temperature is decreased

(*ii*) Pressure is increased by adding N_2 at constant T.

(*a*) (*i*) Towards product, (*ii*) towards reactant

(*b*) (*i*) Towards reactant, (*ii*) no change

(*c*) (*i*) Towards reactant, (*ii*) towards product

(*d*) (*i*) Towards product, (*ii*) no change

26. For the reaction, **[10 April, 2019 (Shift-II)]**

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$,

$\Delta H = -57.2$ kJ mol^{-1} and $K_c = 1.7 \times 10^{16}$

Which of the following statement is INCORRECT?

(*a*) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.

(*b*) The equilibrium will shift in forward direction as the pressure increases.

(*c*) The equilibrium constant decreases as the temperature increases.

(*d*) The addition of an inert gas at constant volume will not affect the equilibrium constant.

Credit:--- Divansh.....

IONIZATION OF ACIDS & BASES, BUFFER SOLUTIONS AND SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

27. Given below are two statements:

Statement-I: Aqueous solution of ammonium carbonate is basic.

Statement-II: Acidic/basic nature of salt solution of a salt of weak acid and weak base depends on K_a and K_b value of acid and the base forming it.

In the light of the above statements, choose the most appropriate answer from the options given below:

[27 Jan, 2024 (Shift-I)]

(*a*) Both Statement-I and Statement-II are correct

(*b*) Statement-I is correct but Statement-II is incorrect.

(*c*) Both Statement-I and Statement-II are incorrect

(*d*) Statement-I is incorrect but Statement-II is correct

28. The pH of an aqueous solution containing 1M benzoic acid ($pK_a = 4.20$) and 1M sodium benzoate is 4.5. The volume of benzoic acid solution in 300 mL of this buffer solution is ________ mL. (given: log2 = 0.3) **[30 Jan, 2024 (Shift-II)]**

29. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate solution will be **[01 Feb, 2024 (Shift-I)]**

30. Solubility of calcium phosphate (molecular mass, M) in water is W_g per 100 mL at 25° C. Its solubility product at 25°C will be approximately. **[01 Feb, 2024 (Shift-II)]**

(*a*) $10^7\left(\frac{W}{M}\right)^3$ (*b*) $10^7\left(\frac{W}{M}\right)^5$

(*c*) $10^3\left(\frac{W}{M}\right)^5$ (*d*) $10^5\left(\frac{W}{M}\right)^5$

31. Given below are two statements:

Statement-I: A Buffer solution is the mixture of a salt and an acid or a base mixed in any particular quantities.

Statement-II: Blood is naturally occurring buffer solution whose pH is maintained by $H_2CO_3/HCO_3^{\ominus}$ concentrations.

In the light of the above statements, choose the correct answer from the options given below.

[08 April, 2024 (Shift-II)]

(*a*) Statement-I is false but Statement-II is true

(*b*) Both Statement-I and Statement-II is true

(*c*) Both Statement-I and Statement-II is false

(*d*) Statement-I is true but Statement-II is false

32. For a sparingly soluble salt AB_2, the equilibrium concentrations of A^{2+} ions and B^- ions are 1.2×10^{-4} M and 0.24×10^{-3} M, respectively. The solubility product of AB_2 is: **[09 April, 2024 (Shift-II)]**

(*a*) 0.069×10^{-12} (*b*) 6.91×10^{-12}

(*c*) 0.276×10^{-12} (*d*) 27.65×10^{-12}

33. Given below are two statements:

Statement-I: On passing $HCl_{(g)}$ through a saturated solution of $BaCl_2$, at room temperature white turbidity appears.

Statement-II: When HCl gas is passed through a saturated solution of NaCl, sodium chloride is precipitated due to common ion effect.

In the light of the above statements, choose the most appropriate answer from the options given below:

[05 April, 2024 (Shift-II)]

(*a*) Statement-I is correct but Statement-II is incorrect

(*b*) Both Statement-I and Statement-II are incorrect

(*c*) Statement-I is incorrect but Statement-II is correct

(*d*) Both Statement-I and Statement-II are correct

34. Given below are two statements:

Statement-I: Methyl orange is a weak acid.

Statement-II: The benzenoid form of methyl orange is more intense/deeply coloured than the quinonoid form.

[8 April, 2023 (Shift-II)]

In the light of the above statement, choose the most appropriate answer from the options given below:

(*a*) Statement-I is correct but Statement-II is incorrect.

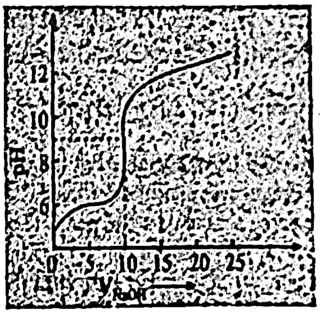
(*b*) Statement-I is incorrect but Statement-II is correct.

(*c*) Both Statement-I and Statement-II are incorrect.

(*d*) Both statement-I and Statement-II are correct.

35. The titration curve of weak acid vs. strong base with phenolphthalein as indictor) is shown below. The $K_{phenolphthalein} = 4 \times 10^{-10}$.

Given: log2 = 0.3



The number of following statements which is/are correct about phenolphthalein is ________ **[8 April, 2023 (Shift-I)]**

A. It can be used as an indicator for the titration of weak acid with weak base.

B. It begins to change colour at pH = 8.4

C. It is a weak organic base

D. It is colourless in acidic medium

36. The solubility product of a sparingly soluble salt A_2X_3 is 1.1×10^{-23}. If specific conductance of the solution is 3×10^{-5} S m^{-1}, the limiting molar conductivity of the solution is $x \times 10^{-3}$ S m^2 mol^{-1}. The value of x is______. **[28 June, 2022 (Shift-I)]**

37. In base vs acid titration, at the end point methyl orange is present as **[25 July, 2022 (Shift-II)]**

(*a*) Quinonoid form (*b*) Heterocyclic form

(*c*) Phenolic form (*d*) Benzenoid form

38. Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

[26 July, 2022 (Shift-II)]

Assertion (A): Phenolphthalein is a pH dependent indicator, remains colourless in acidic solution and gives pink colour in basic medium.

Reason (R): Phenolphthalein is a weak acid. It doesn't dissociate in basic medium.

Credit:--- Divansh.....

In the light of the above statements, choose the *most appropriate* answer from the options given below.

(*a*) Both (A) and (R) are true and (R) is the correct explanation of (A).

(*b*) Both (A) and (R) are true but (R) is NOT the correct explanation of (A)

(*c*) (A) is true but (R) is false

(*d*) (A) is false but (R) is true.

39. A solution is 0.1 M in Cl^- and 0.001 M in CrO_4^{2-}. Solid $AgNO_3$ is gradually added to it. Assuming that the addition does not change in volume and K_{sp} (AgCl) $= 1.7 \times 10^{-10}\ M^2$ and K_{sp} $(Ag_2CrO_4) = 1.9 \times 10^{-12}\ M^3$. **[20 July, 2021 (Shift-II)]**

Select correct statement from the following:

(*a*) Ag_2CrO_4 precipitates first because the amount of Ag^+ needed is low.

(*b*) Ag_2CrO_4 precipitates first as its K_{sp} is low.

(*c*) AgCl will precipitate first as the amount of Ag^+ needed to precipitate is low.

(*d*) AgCl precipitates first because its K_{sp} is high.

40. The pH of ammonium phosphate solution, if pk_a of phosphoric acid and pk_b of ammonium hydroxide are 5.23 and 4.75 respectively, is_______. **[26 Feb, 2021 (Shift-II)]**

41. 0.4 g mixture of NaOH, Na_2CO_3 and some inert impurities was first titrated with $\frac{N}{10}$ HCl using phenolphthalein as an indicator, 17.5 mL of HCl was required at the end point. After this methyl orange was added and titrated. 1.5 mL of same HCl was required for the next end point. The weight percentage of Na_2CO_3 in the mixture is ____. (Rounded – off to the nearest integer) **[25 Feb, 2021 (Shift-I)]**

42. 0.01 moles of a weak acid HA ($K_a = 2.0 \times 10^{-6}$) is dissolved in 1.0 L of 0.1 M HCl solution. The degree of dissociation of HA is ____________ $\times 10^{-5}$. **[17 March, 2021 (Shift-I)]**

(Round off to the nearest integer).

[Neglect volume change on adding HA.

Assume degree of dissociation <<1].

43. 250 mL of 0.5 M NaOH was added to 500 mL of 1 M HCl. The number of unreacted HCl molecules in the solution after complete reaction is_________ $\times 10^{21}$ (Nearest integer) ($N_A = 6.022 \times 10^{23}$) **[20 July, 2021 (Shift-I)]**

44. Given below are two statements. **[26 Aug, 2021 (Shift-I)]**

Statement-I: In the titration between strong acid and weak base, methyl orange is suitable as an indicator.

Statement-II: For titration of acetic acid with NaOH, phenolphthalein is not a suitable indicator.

In the light of the above statements, choose the most appropriate answer from the options given below:

(*a*) Both Statement-I and Statement-II are false

(*b*) Both Statement-I and Statement-II are true

(*c*) Statement-I is true but Statement-II is false

(*d*) Statement-I is false but Statement-II is true

45. The solubility product of $Cr(OH)_3$ at 298 K is 6.0×10^{-3}. The concentration of hydroxide ions in a saturated solution of $Cr(OH)_3$ will be : **[9 Jan, 2020 (Shift-II)]**

(*a*) $(18 \times 10^{-31})^{1/4}$ (*b*) $(4.86 \times 10^{-29})^{1/4}$

(*c*) $(18 \times 10^{-31})^{1/2}$ (*d*) $(2.22 \times 10^{-31})^{1/4}$

46. The molar solubility of $Cd(OH)_2$ is 1.84×10^{-5} M in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12 is: **[12 April, 2019 (Shift-II)]**

(*a*) 6.23×10^{-11} M (*b*) 1.84×10^{-9} M

(*c*) $\frac{2.49}{1.84} \times 10^{-9}$ M (*d*) 2.49×10^{-10} M

47. On decreasing the pH from 7 to 2, the solubility of a sparingly soluble salt (MX) of a weak acid (HX) increased from 10^{-4} mol L^{-1} to 10^{-3} mol L^{-1}. The pK_a of HX is: **[JEE Adv 2023]**

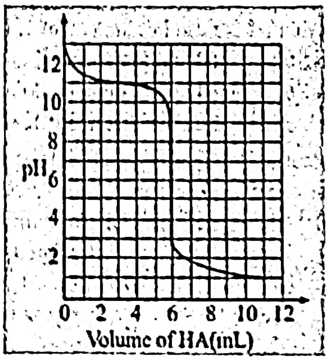
(*a*) 3 (*b*) 4 (*c*) 5 (*d*) 2

48. Concentration of H_2SO_4 and Na_2SO_4 in a solution is 1 M and 1.8×10^{-2} M, respectively. Molar solubility of $PbSO_4$ in the same solution is $X \times 10^{-Y}$ M (expressed in scientific notation). The value of Y is ________.
[Given: Solubility product of $PbSO_4$ (K_{sp}) $= 1.6 \times 10^{-8}$. For H_2SO_4, K_{a_1} is very large and $K_{a_2} = 1.2 \times 10^{-2}$] **[JEE Adv 2022]**

49. 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated against NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permanent faint pink color is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution? **[JEE Adv 2020]**

Exp No.	Vol. of NaOH (mL)
1	12.5
2	10.5
3	9.0
4	9.0
5	9.0

50. A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the pK_b of the base? The neutralization reaction is given by $B + HA \rightarrow BH^+ + A^-$. **[JEE Adv 2020]**



51. An acidified solution of 0.05 M Zn^{2+} is saturated with 0.1 M H_2S. What is the minimum molar concentration (M) of H^+ required to prevent the precipitation of ZnS? Use K_{sp} (ZnS) $= 1.25 \times 10^{-22}$ and overall dissociation constant of H_2S, K_{NET} of $H_2S = K_1K_2 = 1 \times 10^{-21}$. **[JEE Adv 2020]**

PW Challengers

PASSAGE I

Consider 1.0×10^{-7} M solution of sulfuric acid ($K_w = 1.0 \times 10^{-14}$, $K_2 = 1.2 \times 10^{-2}$ at 25 °C). To answer the following questions you may use mass– and charge-balance equations.

1. Calculate $[OH^-]$ (in terms of 10^{-8}) **(Integer Type)**
2. Calculate $[HSO_4^-]$ (in terms of 10^{-12}) **(Integer Type)**

PASSAGE II

The precipitation is widely used in classical methods of the quantitative and qualitative analysis for the separation of ions.

The possibility of separation is determined by the equilibrium concentrations of all species in a solution to be analyzed. Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).

$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-}$ $\quad \log K_1 = -6.50$

$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$ $\quad \log K_2 = 1.36$

3. Calculate the value of equilibrium constants(K_c) of $CrO_4^{2-} + H_2O \rightleftarrows HCrO_4^- + OH^-$ (Answer in terms of 10^{-8}) **(Integer Type)**
4. Calculate the value of equilibrium constants(K_c) of $Cr_2O_7^{2-} + 2OH^- \rightleftarrows 2\,CrO_4^{2-} + H_2O$ (Answer in terms of 10^{-13}) **(Integer Type)**
5. Calculate the pH value of 0.010 M K_2CrO_4 **(Answer upto two decimal place)**
6. Calculate the pH value of 0.010 M $K_2Cr_2O_7$ **(Answer upto two decimal place)**
7. Calculate the pH value of 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COOH (Dissociation constant of acetic acid $K_a = 1.8 \times 10^{-5}$.) **(Answer upto two decimal place)**
8. Consider 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COOH. Calculate the equilibrium concentration (in terms of 10^{-6}) of CrO_4^{2-} in this solution. **(Integer Type)**
9. Calculate the equilibrium concentration (in terms of 10^{-3}) of $Cr_2O_7^{2-}$ in the above solution. **(Integer Type)**

PASSAGE III

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. This will be illustrated by the following calculations:

Lactic acid written as HL is monoprotic, and the acid dissociation constant is

$K_{HL} = 1.4 \times 10^{-4}$.

The acid dissociation constants for carbonic acid are: $K_{a1} = 4.5 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$. All carbon dioxide remains dissolved during the reactions.

10. Calculate pH in a 3.00×10^{-3} M solution of HL. **(Answer upto two decimal place)**
11. Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate. **(Integer Type)**

PASSAGE IV

The equilibrium constant of the reaction $H_2 + I_2 \rightleftharpoons 2\,HI$ is equal to 70.0 (at 500 °C).

12. How much iodine (in %) is converted till the equilibrium is reached if the reactants are mixed in 1 : 1 molar ratio at 500 °C. **(Answer upto one decimal place)**
13. How much iodine (in %) is converted till the equilibrium is reached if the reactants are mixed in 2 : 1 molar ratio at 500 °C. (The amount of di-hydrogen is twice as great as that of di-iodine.) **(Answer upto one decimal place)**
14. How many moles of di-hydrogen should be mixed with one mole of iodine when 99 % of iodine is to be converted to hydrogen di-iodide till the equilibrium is reached at 500 °C? **(Answer upto two decimal place)**

INTEGER TYPE QUESTIONS

15. Calculate the volume (in cm³) of 0.80 M NaOH solution that should be added to a 250 cm³ aqueous solution containing 3.48 cm³ of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. (H_3PO_4 (aq), purity = 85 mass %, density = 1.69 g/cm³, ($pK_1 = 2.15$, $pK_2 = 7.20$, $pK_3 = 12.44$).
16. The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.

Membrane

Stomach $\quad$ Blood

pH = 2.0 $\quad$ pH = 7.4

$H^+ + A^- \rightleftharpoons HA \rightleftharpoons HA \rightleftharpoons H^+ + A^-$

Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. Calculate the ratio of the total concentration ([HA] + [A^-]) of aspirin (acetylsalicylic acid, $pK = 3.52$) in the blood to that in the stomach.

17. A diprotic acid, H_2A, undergoes the following dissociation reactions:

$H_2A \rightleftharpoons HA^- + H^+;\ K_1 = 4.50 \times 10^{-7}$

$HA^- \rightleftharpoons A^{2-} + H^+;\ K_2 = 4.70 \times 10^{-11}$

A 20.00 cm³ aliquot of a solution containing a mixture of Na_2A and NaHA is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode pH meter. Two points on the titration curve are as follows:

cm³ HCl added	pH
1.00	10.33
10.00	8.34

Calculate the total volume (in cm³) of HCl required to reach the second equivalence point. **(Integer Type)**

Credit:--- Divansh.....

ANSWER KEY

CONCEPT APPLICATION

1. (*a*)	2. (*d*)	3. (*d*)	4. (*d*)	5. (*b*)	6. (*a*)	7. (*a*)	8. (*d*)	9. (*a*)	10. (*a*)
11. (*b*)	12. (*a*)	13. (*b*)	14. (*b*)	15. (*c*)	16. (*a*)	17. (*a*)	18. (*a*)	19. (*c*)	20. (*d*)
21. (*d*)	22. (*a*)	23. (*a*)	24. (*b*)	25. (*a*)	26. (*c*)	27. (*c*)	28. (*c*)	29. (*c*)	30. (*c*)
31. (*c*)	32. (*c*)	33. (*b*)	34. (*c*)	35. (*a*)	36. (*b*)	37. (*a*)	38. (*c*)	39. (*d*)	40. (*b*)
41. (*d*)	42. (*b*)	43. (*c*)	44. (*d*)	45. (*b*)	46. (*b*)	47. (*d*)	48. (*b*)	49. (*b*)	50. (*a*)
51. (*c*)	52. (*c*)	53. (*b*)	54. (*d*)	55. (*a*)	56. (*b*)	57. (*a*)			

SCHOOL LEVEL PROBLEMS

1. (*c*)	2. (*c*)	3. (*c*)	4. (*a*)	5. (*d*)	6. (*c*)	7. (*b*)	8. (*c*)	9. (*c*)	10. (*d*)
11. (*b*)	12. (*a*)	24. (i)-(*b*), (ii)-(*a*), (iii)-(*a*), (iv)-(*c*)							

PRARAMBH (TOPICWISE)

1. (*c*)	2. (*d*)	3. (*d*)	4. (*a*)	5. (*d*)	6. (*c*)	7. (*a*)	8. (*b*)	9. (*a*)	10. (*d*)
11. (*a*)	12. (*a*)	13. (*c*)	14. (*b*)	15. (*a*)	16. (*b*)	17. (*c*)	18. (*a*)	19. (*a*)	20. (*a*)
21. (*c*)	22. (*d*)	23. (*c*)	24. (*d*)	25. (*b*)	26. (*d*)	27. (*b*)	28. (*c*)	29. (*b*)	30. (*c*)
31. (*a*)	32. (*b*)	33. (*b*)	34. (*d*)	35. (*b*)	36. (*a*)	37. (*c*)	38. (*d*)	39. (*d*)	40. (*a*)
41. (*a*)	42. (*c*)	43. (*a*)	44. (*b*)	45. (*d*)	46. (*b*)	47. (*c*)	48. (*b*)	49. (*c*)	50. (*c*)
51. (*d*)	52. (*b*)	53. (*a*)	54. (*b*)	55. (*c*)	56. (*c*)	57. (*a*)	58. (*d*)	59. (*c*)	60. (*d*)
61. (*b*)	62. (*a*)	63. (*b*)	64. (*c*)	65. (*c*)	66. (*b*)	67. (*b*)	68. (*b*)	69. (*b*)	70. (*a*)
71. (*a*)	72. (*c*)	73. (*b*)	74. (*b*)	75. (*c*)	76. (*d*)	77. (*b*)	78. (*c*)	79. (*b*)	80. (*b*)
81. (*c*)	82. (*c*)	83. (*a*)	84. (*b*)	85. (*c*)	86. (*c*)	87. (*d*)	88. (*a*)	89. (*c*)	90. (*b*)
91. (*d*)									

PRABAL (JEE MAIN LEVEL)

1. (*a*)	2. (*b*)	3. (*a*)	4. (*b*)	5. (*a*)	6. (*b*)	7. (*b*)	8. (*c*)	9. (*b*)	10. (*a*)
11. (*b*)	12. (*d*)	13. (*c*)	14. (*b*)	15. (*c*)	16. (*a*)	17. (*a*)	18. (*b*)	19. (*d*)	20. (*a*)
21. (*a*)	22. (*a*)	23. (*c*)	24. (*b*)	25. (*b*)	26. (*a*)	27. (*d*)	28. (*b*)	29. (*b*)	30. (*c*)
31. (*a*)	32. (*d*)	33. (*a*)	34. (*a*)	35. (*c*)	36. (*d*)	37. (*a*)	38. (*b*)	39. (*d*)	40. (*c*)
41. (*a*)	42. (*d*)	43. (*c*)	44. (*c*)	45. (*a*)	46. (*a*)	47. (*d*)	48. (*c*)	49. (*b*)	50. (*b*)
51. (*b*)	52. (*a*)	53. (*d*)	54. (*c*)	55. (*b*)	56. (*a*)	57. (*d*)	58. (*b*)	59. (*c*)	60. (*d*)
61. (*c*)	62. (*a*)	63. (*b*)	64. (*d*)	65. (*b*)	66. (*d*)	67. (*a*)	68. (*c*)	69. (*c*)	70. (*a*)
71. (*d*)	72. (*c*)	73. (*a*)	74. (*c*)	75. (*a*)	76. (*a*)	77. (*d*)	78. (*a*)	79. [64]	80. [9]
81. [4]	82. [2]	83. [4]	84. [10]	85. [9]	86. [5]	87. [50]	88. [3]	89. [5]	

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*c*)	2. (*c*)	3. (*a*)	4. (*c*)	5. (*a*)	6. (*c*)	7. (*c*)	8. (*d*)	9. (*b*)	10. (*b*)
11. (*d*)	12. (*c*)	13. (*b*)	14. (*a*)	15. (*a*)	16. (*a*)	17. (*a,c*)	18. (*a,b,c*)	19. (*c,d*)	20. (*c,d*)
21. (*c,d*)	22. (*b,d*)	23. (*b,c,d*)	24. (*a,d*)	25. (*a,c,d*)	26. (*a,b,c*)	27. (*a,c*)	28. (*b,c*)	29. (*a,d*)	30. (*a,b,c*)
31. (*a,d*)	32. (*b,c*)	33. (*c,d*)	34. (*a,b*)	35. (*b*)	36. (*a*)	37. (*b*)	38. (*a*)	39. (*c*)	40. (*b*)
41. (*b*)	42. (*c*)	43. [120]	44. [5]	45. [745]	46. [9]	47. [2]	48. [6]	49. [123]	50. [51]
51. [7.5]	52. [1.6]	53. [5.85]	54. [1.56]	55. [0.0030]					

Credit:--- Divansh.....

PYQ's (PAST YEAR QUESTIONS)

1. [3] **2.** (*d*) **3.** [2] **4.** [417] **5.** [9] **6.** (*a*) **7.** (*b*) **8.** (*c*) **9.** (*d*) **10.** (*c*)
11. (*d*) **12.** [16] **13.** (*c*) **14.** (*a*) **15.** [8.93] **16.** [163] **17.** [12] **18.** [166] **19.** (*c*) **20.** (*a*)
21. [8] **22.** [0.25] **23.** (*a*) **24.** (*d*) **25.** (*b*) **26.** (*a*) **27.** (*a*) **28.** [100] **29.** [7] **30.** (*b*)
31. (*a*) **32.** (*b*) **33.** (*c*) **34.** (*c*) **35.** [2] **36.** [3] **37.** (*a*) **38.** (*c*) **39.** (*a*) **40.** [7]
41. [4] **42.** [2] **43.** [226] **44.** (*c*) **45.** (*a*) **46.** (*d*) **47.** (*b*) **48.** [6] **49.** [0.11]
50. [2.30 to 3.00] **51.** [0.20]

PW CHALLENGERS

1. [4] **2.** [2] **3.** [3] **4.** [4] **5.** [9.25] **6.** [4.20] **7.** [2.87] **8.** [3] **9.** [5] **10.** [3.25]
11. [311] **12.** [80.7] **13.** [95.1] **14.** [6.59] **15.** [103] **16.** [7366] **17.** [28]

> *"The mind is everything.*
> *What you think you become."*
> **– Buddha**

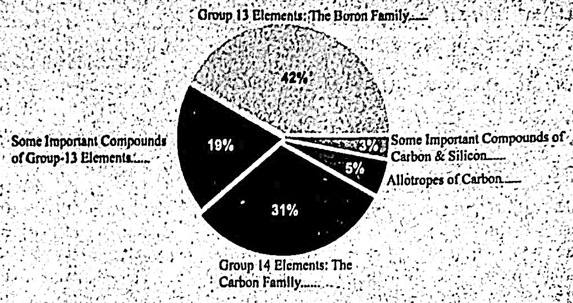
Credit:--- Divansh.....

CHAPTER

9

The p-Block Elements

Topicwise Weightage of JEE Main 6 Years Paper (124 Sets)



"How's the Josb?" for these Topics: *Mark your confidence level in the blank space around the topic (Low-L, Medium-M, High-H)*

INTRODUCTION

The elements in which last electron enters into p-subshell are called as p-block elements. The number of p-orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a p-subshell is six, hence p-block contains six groups. The general electronic configuration of these elements is ns^2np^{1-6} (except for He). There are six groups in p-block.

The first member of each of these groups also displays the ability of forming pπ-pπ bonds to itself (C=C, C≡C, N≡N) and also to other elements of second period (C=O, C≡N, N=O and so on)

Table: General Electronic Configuration and Oxidation state of p-block elements.

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, –4	+3, –3	+4, +2, –2	+5, +3, +1, –1	+6, +4, +2

BORON FAMILY

Group 13 contains six elements: Boron, Aluminium, Gallium, Indium, Thallium and Nihonium.

The heavier members of this group show inert pair effect. Boron compounds, especially the hydrides are electron deficient compounds which can accept a lone pair of electrons hence behave as Lewis acids.

Physical Properties

General electronic configuration is ns^2np^1.

Atomic Number	Atomic Radii	Element Character	Configuration	Metallic
5	85 pm	B	$[He]\ 2s^2\ 2p^1$	Non-metal
13	143 pm	Al	$[Ne]\ 3s^2\ 3p^1$	Metal
31	135 pm	Ga	$[Ar]\ 3d^{10}\ 4s^2\ 4p^1$	Metalloid
49	167 pm	In	$[Kr]\ 4d^{10}\ 5s^2\ 5p^1$	Metal
81	170 pm	Tl	$[Xe]\ 4f^{14}\ 5d^{10}6s^26p^1$	Metal
113	–	Nh	$[Rn]\ 5f^{14}\ 6d^{10}7s^27p^1$	Metal

Electronegativity

Aluminium is most metallic among boron family due to its less electronegativity.

Electronegativity	B	Al	Ga	In	Tl
	2	1.5	1.6	1.7	1.8

Due to poor shielding of 3d and 4d and Lanthanoid contraction

Atomic Size

Atomic size of boron family is smaller than alkaline earth metals and larger than carbon family elements of same period. Down the group atomic size increases irregularly. Gallium is smaller than aluminium due to poor shielding of 3d orbital.

Ionization Energy

Ionization energy decreases from B to Al, but increases from Al to Ga.

Decreasing order of 1st ionization energy is as follows

B > Tl > Ga > Al > In

Oxidation State

$ns^2\,np^1 \rightarrow ns^1\,np_x^{\,1}\,np_y^{\,1}\,np_z^{\,0}$

G.S. E.S.

(a) Normal valency = 3 & oxidation state = ± 3

(b) Generally covalent Compounds are formed by sp^2 hybridisation and have trigonal planar geometry.

(c) Compounds of B are more covalent than compounds of Al because charge/size ratio of B is more than Al.

(d) The charge density of B is greater hence greater polarising power, therefore more covalent character in Boron compound is observed.

(e) B → Tl Covalent character decreases due to decrease in charge density or polarising power.

(f) Trivalent compounds of group 13 are electron deficient eg. BF_3 acts as a lewis acid.

(g) In general B shows oxidation state of +3 and –3
eg. Mg_3B_2 the oxidation state of B is –3.
BF_3 the oxidation state of B is +3.

(h) $6s\,e^-$ of Tl {Inert pair effect} are same as duplet configuration of He and so $6s\,e^-$ resist to take part in bonding.

(i) Tl has valency = 1, 3 & oxidation state = +1 & +3.

(j) Tl^{+3} is strong oxidising agent.

(k) Tl^{+3} is highly unstable.

(l) Tl^+ Compounds resemble compounds of alkali metals Thallous compounds Tl^{+1} will be more stable as compared to Tallic compounds (Tl^{+3})

(m) Ga, In, Tl show inert pair effect in their compounds.

(n) Indium in +1 oxidation state is reducing agent.

Melting and Boiling Points

(a) B has very high melting point & boiling point due to giant molecular structure.
B.p. order : B > Al > In > Tl > Ga
M.p. order : B > Al > Ga < In < Tl

(b) Ga has least melting point among all these.

(c) Ga exists in liquid state in summer (m.p. = 303K)

(d) Main use of Ga is in high temperature thermometry.

Train Your Brain

Example 1: The stable oxidation state of Tl is +1 hence its hydroxide is similar to:

(*a*) $Ca(OH)_2$ (*b*) $Al(OH)_3$

(*c*) $Mg(OH)_2$ (*d*) NaOH

Sol. **(*d*)** Inert pair effect

Example 2: Choose the incorrect option.

(*a*) Tendency of formation of ionic compound increases from B to Tl.

(*b*) Boron forms only covalent compound.

(*c*) Thallium forms only ionic compounds.

(*d*) Group 13 elements have less tendency to form complexes than the s-block elements.

Sol. **(*d*)** Group 13 element have more tendency to form complex than s-block element due to their small size, more effective nuclear charge as well as vacant orbitals to accept electrons.

Example 3: Boron cannot form which one of the following anions?

(*a*) $B(OH)_4^-$ (*b*) BO_2^- (*c*) BF_6^{3-} (*d*) BF_4^-

Sol. **(c)** Boron cannot form BF_6^{3-} anions due to absence of 2d orbitals in boron. hence, it cannot expand its octet. BF_6^{3-} anion will have 12 valence electrons around B.

Example 4: Melting point is higher for

(*a*) B (*b*) Al (*c*) Ga (*d*) In

Sol. **(*a*)** B has very high melting point and boiling point due to giant molecular structure.

M.p. order: B > Al > Ga < In < Tl

Concept Application

1. The increasing order of atomic radii of the following group 13 elements is:

   (*a*) Al < Ga < In < Tl (*b*) Ga < Al < In < Tl

   (*c*) Al < In < Ga < Tl (*d*) Al < Ga < Tl < In

2. **Statement-I:** Boron always forms covalent bond

   Because:

   Statement-II: The small size of B^{3+} favours formation of covalent bond.

   (*a*) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I

   (*b*) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-I

   (*c*) Statement-I is True, Statement-II is False

   (*d*) Statement-I is False, Statement-II is True

Credit:--- Divansh.....

3. Boron compounds behave as Lewis acids because of their
   (*a*) Acidic nature
   (*b*) Covalent nature
   (*c*) Electron deficient character
   (*d*) Ionising property
4. Boron has an extremely high melting point because of:
   (*a*) The strong vander Waals forces between its atoms
   (*b*) The strong binding forces in the covalent polymer
   (*c*) Its ionic crystal structure
   (*d*) Allotropy
5. Which one of the following has the lowest m.p.?
   (*a*) B (*b*) Al (*c*) Ga (*d*) Tl

CHEMICAL PROPERTIES

1. **Reactivity towards air:** Amorphous boron and aluminium metal on heating in air forms trioxide and forms nitride at very high temperature. Gallium and indium are not affected with air while thallium does.

   B_2O_3 – Acidic oxide

   Al_2O_3, Ga_2O_3 – Amphoteric oxide

   In_2O_3, Tl_2O_3 – Basic oxide

   $4E(s) + 3O_2(g) \rightarrow 2E_2O_3(s)$

   $2E(s) + N_2(g) \rightarrow 2EN(s)$ (Where E = B, Al, Ga, In, Tl)

   B_2O_3 is called boric anhydride as it is anhydride of boric acid.

2. **Reactivity towards acids:** Boron is not affected by non-oxidising agents like HCl and dil. H_2SO_4 while all other elements react with conc. H_2SO_4 and HNO_3. Ga and Al develop protective layer of oxide with conc. HNO_3.

   $2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$

   $2B(s) + 3H_2SO_4(aq) \rightarrow 6H^+(aq) + 2BO_3^{-3}(aq) + 3SO_2(g)$

   $B(s) + 3HNO_3(aq) \rightarrow 3H^+(aq) + BO_3^{-3}(aq) + 3NO_2(g)$

3. **Reactivity towards alkalies:** Except Indium and Thallium all other elements react with alkali solutions

   $2M(s) + 2NaOH(aq) + 2H_2O \rightarrow 2NaMO_2(s) + 3H_2(g)$

   (M= Al or Ga)

   Example, Al also reacts with aq. Alkali and liberates dihydrogen.

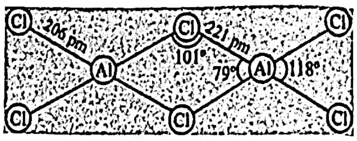
   $2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na^+ [Al(OH)_4]^-(aq) + 3H_2(g)$

   Sodium tetrahydroxoaluminate (III)

4. **Reactivity towards halogens:** Trihalides are formed when these elements react with halogens. Mostly these halides exist as discrete molecular species which are sp^2 hybridised and covalently bonded. TlI_3 (Tl^{3+} I^-) is unstable but TlI_3 (Tl^+ I_3^-) can exist.

   $AlCl_3$ achieves stability by forming a dimer.

Credit:--- Divansh.....



(*i*) Al_2O_3 on heating with coke & Cl_2 forms Al_2Cl_6 and this reaction is called as **Reductive Chlorination.**

$Al_2O_3 + 3C + 3Cl_2 \rightarrow Al_2Cl_6 + 3CO$.

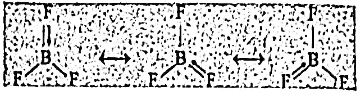
(*ii*) Acidic strength is inversely proportional to back-bonding, as back-bonding decreases from BF_3 to BI_3 as given below

$BF_3 > BCl_3 > BBr_3 > BI_3$ (back bonding)

Hence, Lewis acidic strength will increase as under

$BF_3 < BCl_3 < BBr_3 < BI_3$

pπ-pπ back-bonding is strongest in BF_3 because both B and F involve 2p orbital in back-bonding.



(*iii*) Al, Ga, In & Tl do not show back bonding because of increase in the size of the element. Actually they make use of vacant p-orbitals to complete their octet by forming dimers.

(*iv*) Stability of halides in +3 oxidation state decreases down the group.

FACTS ABOUT ALUMINIUM CHLORIDE ($AlCl_3$)

Key Note

- Anhydrous $AlCl_3$ can be prepared by passing dry Cl_2 or HCl gas over hot Al. It may also be prepared by passing dry Cl_2 gas over a hot mixture of alumina & Coke (McAfee process).
- Anhydrous $AlCl_3$ is hygroscopic in nature & form $AlCl_3.6H_2O$ which is deliquiscent in nature.
- Anhydrous $AlCl_3$ gives out HCl fumes when exposed to moist air (due to rapid hydrolysis).
- In organic solvents, $AlCl_3$ exists as a dimer Al_2Cl_6.
- In $AlCl_3$, Al is sp^2 hybridised while in Al_2Cl_6 its state of hybridisation is sp^3.
- $AlCl_3$ does not conduct current in the fused state.

Train Your Brain

Example 5: Boron reacts with nitric acid to form:

(*a*) Sodium borate, H_2
(*b*) Boric acid
(*c*) Diborane
(*d*) Borax

Sol. (*b*) $B + 3HNO_3 \longrightarrow \underset{\text{Boric acid}}{H_3BO_3}$

Example 6: Which of the following compounds are formed when boron trichloride is treated with water?

(*a*) $H_3BO_3 + HCl$
(*b*) $B_2H_6 + HCl$
(*c*) $B_2O_3 + HCl$
(*d*) None of these

Sol. (*a*) $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$

Except BF_3 all tri halides are readily Hydrolysided by water.

Concept Application

6. Heating an aqueous solution of aluminium chloride to dryness will give:
(*a*) $AlCl_3$
(*b*) Al_2Cl_6
(*c*) Al_2O_3
(*d*) $Al(OH)Cl_2$

7. Aluminium is industrially prepared from:
(*a*) Fused cryolite
(*b*) Bauxite ore
(*c*) Alunite
(*d*) Borax

8. Aluminium is not acted upon by pure water as –
(*a*) Impurities in water are essential for the reaction to occur.
(*b*) It is light metal.
(*c*) It is protected by a film of aluminium oxide.
(*d*) It is not a reactive metal.

IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Trihalides of these elements are covalent in nature and are hydrolysed in water and produces species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$ (except in boron).

$$\ddot{N}H_3 + BF_3 \longrightarrow H_3\overset{+}{N} - \overset{-}{B}F_3$$

In this reaction, hybridisation of BF_3 changes to sp^3 as one more bond is formed with nitrogen.

$BF_3 + HF \longrightarrow H^+ [BF_4]^-$

Here F^- reacts with BF_3 as F^- is nucleus-loving (nucleophile) and H^+ is electron-loving (electrophile) and BF_3 itself wants electrons.

$[BF_4]^-$ is a complex anion and it is having sp^3 hybridisation with tetrahedral geometry.

Due to absence of d-orbital maximum covalency of B is 4 while other elements of the group have valence d-orbitals hence, maximum covalency can be expected beyond 4.

SOME IMPORTANT COMPOUNDS OF BORON

1. **Borax or Tincal**

(*i*) Common Indian name is Suhaga.

(*ii*) $Na_2B_4O_7.5H_2O$ is known as Jeweller's Boron, also named as sodium tetra borate penta hydrate.

(*iii*) $Na_2B_4O_7$ is known as Boron glass.

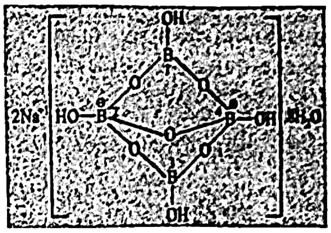
Preparation form Colemanite

$Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\Delta} 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$

Borax is a white crystalline solid and can be prepared by boric acid.

$4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$

Formula: $Na_2B_4O_7.10H_2O$ or $Na_2[B_4O_5(OH)_4].8H_2O$



Number of B in sp^2 hybridisation = 2 (1, 3)

Number of B in sp^3 hybridisation = 2 (2, 4)

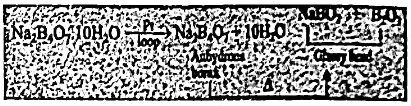
Oxidation state of all boron present = +3 state

Number of B—O—B bonds = 5

Number of B—O bonds = 14

Number of bridging oxygen between two boron = 5

On heating borax first loses water molecules and swells up and gives sodium metaborate which on further heating turns into a transparent liquid which solidifies into glassy bead. It is also called **borax bead test.**



This glassy bead reacts with CuO or CoO to give blue bead and reacts with TiO to give yellow bead of metaborate.

Glassy bead + CuO $\rightarrow \underset{\text{Blue bead}}{Cu(BO_2)_2}$

Glassy bead + CoO $\rightarrow \underset{\text{Blue bead}}{Co(BO_2)_2}$

Glassy bead + TiO $\rightarrow \underset{\text{Yellow bead}}{Ti(BO_2)_2}$

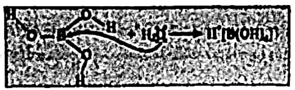
Colour of meta borates

Cu and Co-Blue; Fe and Cr-Green; Ni-Brown.

Borax bead test is used for identification of metal cations which form colored meta borates.

2. **Orthoboric acid (H_3BO_3):** It is white, soft, needle-like crystals having a soapy touch.

It does not give $3H^+$ but accepts one lone pair from H_2O, so n-factor = 1. This is a monobasic Lewis acid as oxygen of $H_2\ddot{O}$ gives one electron pair to boron, so it acquires positive charge and becomes unstable, so it furnishes one H^+ and gets stable.



In $H^+[B(OH)_4]^-$ hybridisation of boron is sp^3.

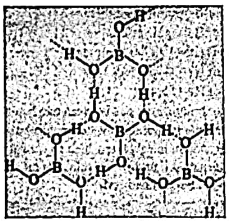
It is prepared by treating concentrated sulphuric acid with borax.

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$

On heating to 100°C it gives metaboric acid which on further heating to 160°C gives $H_2B_4O_7$ which on extremely high temperature gives boric oxide.

$$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 + H_2O \uparrow$$

$$H_3BO_3 \xrightarrow{160^\circ C} \underset{\text{Tetraboric Acid}}{H_2B_4O_7} \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$$



Structure of boric acid; the dotted lines represent hydrogen bonds.

Boric acid is layered structure. $B(OH)_3$ units are joined by hydrogen bonds and form two dimensional sheet.

Reaction with ethanol

$$H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{Triethyl borate}}{(C_2H_5O)_3B} + 3H_2O$$

(green edged flame.)

This is also called an Alcohol test.

Uses

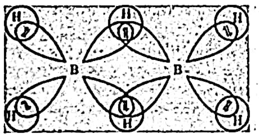
(*i*) As a antiseptic, as eye wash (eye-lotion) and as food preservatives.

(*ii*) In leather - industry.

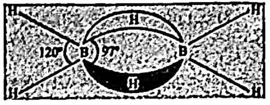
(*iii*) In the preparation of glass and enamels.

3. Hydrides of boron

B_2H_6 (Diborane)

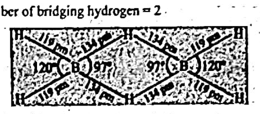


It involves 3 centre 2 electron bonding called banana bonding or bridge bonding.



Number of terminal hydrogen = 4

Number of bridging hydrogen = 2



Number of bonds of bond length 119 pm = 4

Number of bonds of bond length 134 pm = 4

Maximum number of atoms present in same plane = 6

Preparations of Diborane:

(*i*) $3LiAlH_4 + 4BF_3 \rightarrow 2B_2H_6 + 3AlF_3 + 3LiF$

(*ii*) $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

(*iii*) $6NaH + 2BF_3 \xrightarrow{450K} B_2H_6 + 6NaF$

Since boranes have vacant p-orbitals in central boron atom hence, it reacts with water and thus shows hydrolysis.

$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$

Boron hydride reacts with excess ammonia to give $B_2H_6.2NH_3$ which is white ionic solid and consists of $[H_3N \rightarrow BH_2 \leftarrow NH_3]^+$ and $[BH_4]^-$.

When boron hydride reacts with excess ammonia at higher temperature then it gives boron nitride that has graphite-like structure $(BN)_n$ but when diborane and ammonia react in ratio 1 : 2 at higher temperature then it gives borazine $(B_3N_3H_6)$ which is known as **inorganic benzene** or **borazine.**

Train Your Brain

Example 7: Products formed are

$2NaBH_4 + I_2 \xrightarrow{\text{Polyether}}$

(*a*) HI, NaI and H_2 (*b*) B_2H_6, NaI and HI

(*c*) B_2H_6, NaI and H_2 (*d*) $H_3BO_3 + H_2$

Sol. (*b*) $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

Example 8: Which type of hydride is BH_3?

(*a*) Electron deficient (*b*) Electron precise

(*c*) Electron excess (*d*) Lewis base

Sol. (*a*) Octet of boron is incomplete therefore it is Electron deficient and Lewis acid.

Example 9: Which of the following statement is correct regarding B_2H_6?

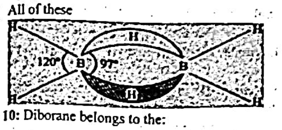
(*a*) Each boron atom is sp^3 hybridised

(*b*) B_2H_6 is electron deficient

(*c*) B_2H_6 has banana bond

(*d*) All of these

Sol. (*d*)



Example 10: Diborane belongs to the:

(*a*) B_nH_{n+6} series (*b*) B_nH_{n+1} series

(*c*) B_nH_{n+4} series (*d*) B_nH_{n+8} series

Sol. (*c*) Boranes having general formula of B_nH_{n+4} are called nidoboranes.

Example 11: Complete the following reactions and identify the products formed.

(*a*) $BCl_3 + NH_4Cl \xrightarrow[C_6H_5Cl]{140^\circ C} (A) \xrightarrow{NaBH_4} (B)$

(*b*) $BCl_3 + H_2 + C_{fibre} \xrightarrow{1700-1800^\circ C}$ product(s)

Sol. (*a*) $3BCl_3 + 3NH_4Cl \xrightarrow[C_6H_5Cl]{140^\circ C} B_3N_3H_3Cl_3$

$\xrightarrow{NaBH_4} B_3N_3H_6$ (borazine)

(*b*) $4BCl_3 + 6H_2 + C_{fibre} \xrightarrow{1700-1800^\circ C} B_4C_{(fibre)} + 12\,HCl$

Concept Application

9. An aqueous solution of borax is:
   (*a*) Neutral (*b*) Amphoteric
   (*c*) Basic (*d*) Acidic
10. The type of hybridisation of boron in diborane is
   (*a*) sp (*b*) sp^2
   (*c*) sp^3 (*d*) dsp^2

ALUMS

Alums are double sulphates with their general formula as $M_2SO_4.M'_2(SO_4)_3.24H_2O$ where

M = Mono valent radical like Na^+, K^+, NH_4^+ &

M' = Trivalent radicals like Al^{+3}, Cr^{+3}, Fe^{+3} etc.

The Different Alums are

(*i*) Potash alum: $K_2SO_4.Al_2(SO_4)_3.24H_2O$

(*ii*) Chrome Alum: $K_2SO_4.Cr_2(SO_4)_3.24H_2O$

(*iii*) Ammonium Alum: $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

(*iv*) Iron Alum: $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$

Key Note

(*i*) Li does not form Alum because size of Lithium ion is too small and it can not have a Coordination number of six.

(*ii*) In alums each metal ion is surrounded by six water molecules. eg. $[M(H_2O)_6]^+$, $[M'(H_2O)_6]^{3+}$

Important Points

(*a*) All Alums are isomorphous.

(*b*) On heating it loses its water of crystallization and swells up. eg.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{200^\circ C} K_2SO_4 + Al_2(SO_4)_3 + 24H_2O$$

$$K_2SO_4 \cdot Al_2(SO_4)_3 \xrightarrow{\text{Red Heat}} K_2SO_4 + Al_2O_3 + 3SO_3$$

(c) These are highly acidic in aq. solution.

(*d*) **Pseudo alums:** Double sulphates of divalent ions and trivalent ions with 24 water molecules in their crystals are known as pseudo alums.

eg. $MSO_4 \cdot M_2'(SO_4)_3 \cdot 24H_2O$

Where M = divalent or Bivalent

M' = Trivalent metal

Uses of Boron and It's compounds: Boron is a hard solid having high melting point low density and very low electrical conductivity. Some important boron compounds are:

(*a*) **Boron fibers:** It is mixed with plastic to form a material which is lighter than aluminium but tougher and stiffer than steel hence it is used in body armour, missiles and aircrafts.

(*b*) **Boron-10 (B^{10}) isotope:** Boron carbide rods or boron steel are used to control nuclear reactions as neutron absorbers.

$${}_5B^{10} + {}_0n^1 \rightarrow {}_5B^{11}$$

(c) **Borax:** It is used in manufacture of enamels and glazes for pottery and tiles. It is also used in making optical glasses and borosilicate glasses (which is very resistant to heat and shock). Borax is also used as an antispectic.

(*d*) **Boric acid:** It is used in glass industry, in food industry as preservative. It is also used as an antiseptic and eye wash under the name 'boric lotion'. It is also used in manufacture of enamels and glazes for pottery.

(*e*) **Boron carbide(B_4C):** It is hardest boron compound and used in bullet proof vest and as abrasive in polishing.

Uses of Aluminium and It's compounds: Aluminium and its alloy are used in packing industry, utensil industry, aeroplane and transportation industry etc.

1. **Alumina (Al_2O_3)**
   (*a*) Used in chromatography (as adsorbent).
   (*b*) Used in making bauxite bricks which are used for lining furnaces.
2. **Aluminium chloride ($AlCl_3$):** Used in manufacture of dyes, drugs and perfumes and also in manufacture of gasoline. It is also used as catalyst in Friedel Craft reaction.
3. **Potash Alum**
   $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$ or $2[KAl(SO_4)_2 \cdot 12H_2O]$
   Used in purification of water, leather tanning, as antiseptic and as a mordant.

Key Note

(*i*) Use of aluminium and its compounds for domestic purposes is now reduced considerably because of their **toxic** nature.

(*ii*) Ultramarine is a compound of aluminium which is an artificial **Lapis-Lazuli** (rare mineral having fine blue colour). It is a complex silicate of sodium and aluminium having 12% of sulphur which is used in calico printing and in making blue paints.

Train Your Brain

Example 12: Which one of the following is the correct statement

(*a*) Boric acid is a protonic acid.

(*b*) Beryllium exhibits coordination number of six.

(*c*) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase.

(*d*) $B_2H_6 \cdot 2NH_3$ is known as "inorganic benzene".

Sol. (*c*) Inorganic benzene is $B_3N_3H_6$. Boric acid is a weak mono basic Lewis acid and beryllium exhibits co-ordination number of 4 only. $BeCl_2$ and $AlCl_3$ both exhibit bridged structures in the solid state.

Example 13: The correct statement for orthoboric acid is/are

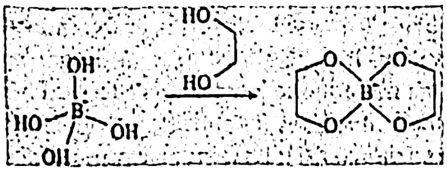
(*a*) It behaves as a weak acid in water due to self ionization

(*b*) Acidity of its aqueous solution increases upon addition of ethylene glycol

(*c*) It has a three dimensional structure due to hydrogen bonding.

(*d*) It is a weak electrolyte in water

Sol. $H_3BO_3 + 2H_2O \rightleftharpoons H_3O^+ + B(OH)_4^-$



⇒ On addition of glycol, equilibrium shift in forward direction ⇒ it's acidity increases.

Example 14: In which of the following compounds banana bond is present?

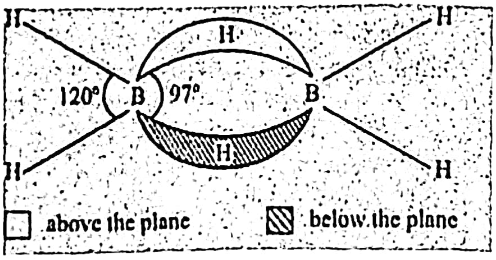
(*a*) BCl_3

(*b*) B_2H_6

(*c*) $B(OH)_3$

(*d*) All of these

Sol. (*b*)



Example 15: H_3BO_3 is

(*a*) Monobasic and weak Lewis acid
(*b*) Monobasic and weak Bronsted acid
(*c*) Monobasic and strong Lewis acid
(*d*) Tribasic and weak Bronsted acid

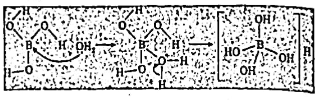
Sol. (*a*) $H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$
(Monobasic weak Lewis Acid)

Example 16: Statement-I: In water, orthoboric acid behaves as a weak monobasic acid.

Statement-II: In water, orthoboric acid acts as a proton donor.

(*a*) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I
(*b*) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-I
(*c*) Statement-I is True, Statement-II is False
(*d*) Statement-I is False, Statement-II is True

Sol. (*c*)



Concept Application

11. In alums, each metal ion is surrounded by
(*a*) Two water molecules
(*b*) Four water molecules
(*c*) Six water molecules
(*d*) Eight water molecules

12. When a solution of sodium hydroxide is added in excess to the solution of potash alum, we obtain
(*a*) A white precipitate
(*b*) Bluish white precipitate
(*c*) A clear solution
(*d*) A crystalline mass

13. Which of the following is not an ionic trihalide?
(*a*) AlF_3 (*b*) BF_3
(*c*) InF_3 (*d*) GaF_3

GROUP 14 ELEMENTS: THE CARBON FAMILY

Group IV A contains six elements: Carbon, Silicon, Germanium, Tin, Lead and Flerovium.

General electronic configuration is ns^2np^2.

All elements of this family except carbon have tendency to show maximum covalency of six due to absence of vacant d-orbitals.

Silicon is (27.7%). Carbon is the seventeenth most abundant element in earth crust. Carbon is important element of all living organisms. Till yet more than 5 million organic compounds have been discovered, and about 40,000 new organic compounds are being discovered every year.

Key Note

Most abundant element in earth crust is oxygen (46.6%) by mass. Second most abundant element is silicon (27.7%). Third most abundant element is aluminium (8%) and fourth most abundant element is iron.

Silicon is used in cement, glass, transistors, semiconductors. Tin is used in alloys. Tin mainly occurs as cassiterite (SnO_2) and lead occurs as galena (PbS).

Germanium is used in transistors.

Lead is used in glass, paints and varnish.

Physical Properties

Atomic Number	Element	Atomic radii (pm)	Electronic configuration	Metallic character
6	C	77	[He] $2s^2 2p^2$	Non-metal
14	Si	117	[Ne] $3s^2 3p^2$	Metalloid
32	Ge	122	[Ar] $3d^{10}4s^2 4p^2$	Metalloid
50	Sn	140	[Kr] $4d^{10} 5s^2 5p^2$	Metals
82	Pb	146	[Xe] $5d^{1}4f^{4}6s^{2}6p^{2}$	Metals
114	Fl	[illegible]	[Rn] $6d^{10}5f^{14}7s^27p^2$	Metals

The elements of this group form covalent bonds with each other and therefore there are strong binding forces between their atoms in both solid and liquid states.

Consequently the melting and boiling points of group 14 elements are much higher in comparison to corresponding to group 13 elements. The atomic radius, ionic radius and density increase when one moves from top to bottom in a group in periodic table.

Atomic Size: Size of this family is smaller than boron family but larger than nitrogen family, and down the group atomic size increases regularly. There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb, a small increase in radius is observed. This is due to the presence of completely filled d & f orbitals in heavier members.

Still properties of silicon differs from germanium due to poor shielding effect of 3d subshell and properties of germanium differs from tin due to poor shielding effect of 4f subshell (Lanthanoid contraction).

Properties of tin are different from lead due to poor sheilding effect of 5f subshell (Actinoid contraction).

Ionization Energy and Electronegativity: Ionization energy of this group is higher than boron family and lower than nitrogen family. Down the group ionization energy decreases irregularly.

Decreasing order of first ionization energy is as follows:

C > Si > Ge > Pb > Sn

ization energy increases from Sn to Pb, it increases slightly due to Lanthanide contraction and increase of 32 units of nuclear charge in Pb over Sn.

Element	Electronegativity	
C	2.5	
Si	1.8	three members have same electronegativity
Ge	1.8	
Sn	1.8	
Pb	1.9	

Order of electronegativities is C > Pb > Si = Ge = Sn

Catenation: Catenation power of carbon family is higher than boron family and nitrogen family. Down the group, catenation tendency decreases.

Decreasing tendency of catenation is as follows:

C >> Si > Ge = Sn, (Pb do not show catenation).

Oxidation State: They can form M^{+4} or M^{-4} ions. But due to high I.E., they do not form M^{+4}. C and Si show +4 oxidation state while Ge, Sn and Pb shows +4 as well as +2 oxidation state.

Chemical Properties

1. **Reactivity towards air:** All members of this group form monoxide of the general formula MO such as CO, SiO, SnO and PbO. All members of this group form dioxides of molecular formula MO_2 such as CO_2, SiO_2, GeO_2, SnO_2 and PbO_2.

   CO_2 is monomeric, SiO_2 is 3-D network solid.

   Dioxides CO_2, SiO_2 and GeO_2 are acidic whereas dioxides SnO_2 and PbO_2 and mono-oxides SnO and PbO are amphoteric. Mono-oxide CO is neutral while GeO is distinctly acidic.

2. **Reactivity towards water:** In this family carbon, silicon and germanium are unaffected by water while lead becomes inert towards water due to formation of protective oxide film. Tin is converted into tin dioxide and hydrogen gas is liberated on reaction with steam.

   $Sn + 2H_2O(g) \rightarrow SnO_2 + 2H_2$

3. **Reactivity towards halogen:** On moving down the group from carbon to lead, stability of +4 oxidation state decreases while stability of +2 oxidation state increases and hence oxidising power decreases down the group due to inert pair effect.

   These elements form two types of halides - MX_2 and MX_4. Most of the MX_4 are covalent. SnF_4 and PbF_4 are ionic in nature.

   Thermal stability decreases with increasing atomic size or molecular mass of tetrahalide or due to decreasing polarity.

   $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$

   $CF_4 > CCl_4 > CBr_4 > CI_4$

Key Note

PbI_4 is not stable as I^- is strong reducing agent which reduces Pb^{+4} to Pb^{+2} and also stability of +4 oxidation state of Pb is lesser than +2 state.

$PbI_4 \rightarrow PbI_2 + I_2$

Hydrolysis of Halides

The chlorides except CCl_4 are hydrolysed readily by water

$$SiCl_4 + H_2O \rightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$

Hydrolysis of silicon tetrafluoride gives silica and fluorosilicic acid

$$3SiF_4 + 4H_2O \rightarrow \underset{\text{(Silica)}}{Si(OH)_4} + \underset{\text{(Fluorosilicic acid)}}{2H_2SiF_6}$$

Due to unavailability of vacant d-orbitals, carbon tetrahalides cannot increase its co-ordination number hence does not form complexes while those having vacant d-orbitals form.

ANOMALOUS BEHAVIOUR OF CARBON

Carbon shows anomalous behaviour due to its smaller size, higher electronegativity, higher ionization enthalpy and unavailability of d-orbitals.

Carbon atom forms double or triple bonds involving pπ-pπ bonding. Carbon also has the property to form closed chain compounds with O, S and N atoms as well as it forms pπ-pπ multiple bonds with other elements particularly N, S and O.

CCl_4 is stable, while other chloride can hydrolyse due to presence of vacant d-orbital.

Train Your Brain

Example 17: The tendency for catenation in the group 14 elements is in the order:

(*a*) $C <<< Si < Ge <<<< Sn < Pb$

(*b*) $C >>> Si > Ge >>> Sn > Pb$

(*c*) $C <<< Si < Ge \simeq Sn < Pb$

(*d*) $C >>> Si > Ge \simeq Sn >>> Pb$

Sol. (*d*) $C >> Si > Ge \simeq Sn >>> Pb$

Small size of carbon

Example 18: The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence:

(*a*) $GeX_2 << SiX_2 << SnX_2 << PbX_2$

(*b*) $SiX_2 << GeX_2 << PbX_2 << SnX_2$

(*c*) $SiX_2 << GeX_2 << SnX_2 << PbX_2$

(*d*) $PbX_2 << SnX_2 << GeX_2 << SiX_2$

Sol. (*b*) Due to the inert pair effect (the reluctance of ns^2 electrons of outermost shell to participate in bonding) the stability of M^{2+} ions (of group IV elements) increases as we go down the group.

The stability of dihalides increases down the group:

$SiX_2 < GeX_2 < PbX_2 < SnX_2$

Concept Application

14. Which element-element bond has the highest bond dissociation energy?

(*a*) C–C (*b*) Si – Si

(*c*) Ge – Ge (*d*) Sn – Sn

15. Solid CO_2 is known as dry ice, because

(*a*) It melts at 0°C

(*b*) It evaporates at 40°C

(*c*) It evaporates at –78°C without melting

(*d*) Its boiling point is more than 199°C

16. CCl_4 is used as a fire extinguisher because

(*a*) Its m.p. is high

(*b*) Its forms covalent bond

(*c*) Its b.p. is low

(*d*) It gives incombustible vapours.

17. What is the correct order of I.E.?

(*a*) $C < Si < Ge < Pb < Sn$

(*b*) $C > Si > Pb > Ge > Sn$

(*c*) $C > Si > Ge > Sn < Pb$

(*d*) $C > Si > Ge > Sn > Pb$

18. In view of the signs of $\Delta_rG°$ for the following reactions

$PbO_2 + Pb \rightarrow 2\,PbO,\ \Delta_rG° < 0$

$SnO_2 + Sn \rightarrow 2\,SnO,\ \Delta_rG° > 0,$

Which oxidation states are more characteristic for lead and tin?

(*a*) For lead + 4, for tin + 2

(*b*) For lead + 2, for tin + 2

(*c*) For lead + 4, for tin + 4

(*d*) For lead + 2, for tin + 4

19. The metallic character of group-14:

(*a*) Decreases from top to bottom

(*b*) Increases from top to bottom

(*c*) Dose not change gradually

(*d*) Has no significance

ALLOTROPES OF CARBON

All the elements of the carbon family with the exception of lead exhibit allotropy and this tendency decreases from C to Pb. It is due to decreasing bond energy.

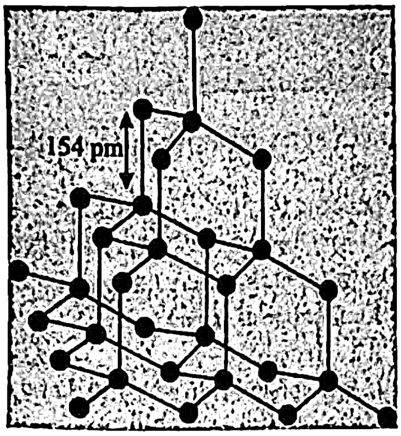
Bond	C—C	Si—Si	Ge—Ge	Sn—Sn
Bond energy (kJ/mol)	348	297	260	240

Carbon shows allotropism due to catenation and pπ-pπ bond formation. Carbon exists in two allotropic forms - crystalline and amorphous. The crystalline forms are diamond and graphite while the amorphous forms are coal, charcoal and lamp-black. The third crystalline form is fullerenes discovered by Kroto, Smalley and Curl.

Tin has maximum number of allotropes.

DIAMOND

In diamond each carbon is joined to other four carbon tetrahedrally and carbon-carbon bond length is 1.54A° and bond angle is 109°28' having sp^3 hybridisation on each carbon. All four electrons in carbon are involved in bonding hence, it is bad conductor of electricity



The structure of diamond

It is purest form of carbon and hardest natural substance known. It is transparent and has a specific gravity 3.52 and its refractive index is high (2.45).

(*i*) 1 carat of diamond = 200 miligram.

(*ii*) Diamond powder if consumed is fatal and causes death in minutes.

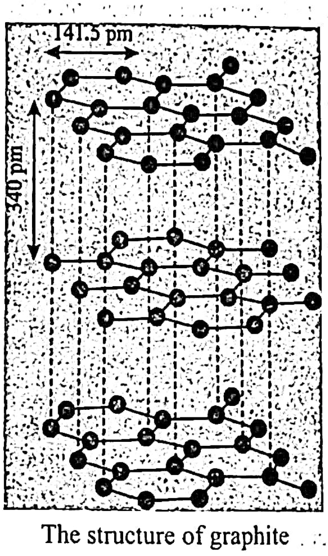
It is difficult to break due to extented covalent bonding.

Diamond is used for making cutters. Blades of diamond are used in eye surgery and as an abrasive for sharpening hard tools. Impure diamonds (black) are used in knives for cutting glass.

GRAPHITE

Each carbon is sp^2 hybridised. It has layered structure. These layers are attracted by van der Waals force. Each carbon has one free electron in p-orbital, so it is a good conductor of electricity. All electrons get delocalized in one layer and form π-bond. Graphite is aromatic. Electron jumps from one orbital to another hence it is a good conductor of heat and electricity. In graphite carbon-carbon bond length is 141.5 pm and distance between adjacent graphite layer is 340 pm.

Graphite is used as a lubricant at high temperature. Oil gets burn or denatured at high temperature but graphite does not get denature even at high temperature so, preferred over oil and grease.



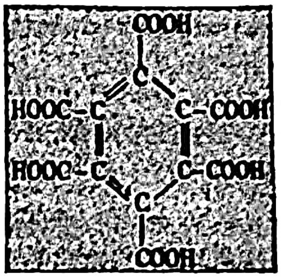
The structure of graphite

Graphite marks the paper black so it is called Black lead or plumbago and so it is used in pencil lead.

Composition of pencil lead is graphite + clay. The percentage of lead in pencil lead = 0%.

Graphite has high melting point so it is employed in manufacture of crucible.

Graphite when heated with oxidising agents like alkaline $KMnO_4$ forms mellitic acid.



Benzene hexa carboxylic acid

Graphite on oxidation with conc. HNO_3 gives acid i.e. known as **Graphite acid ($C_{12}H_6O_{12}$).**

Important points: Graphite is of two forms : α and β.

In α-graphite, layers are arranged in sequence ABAB... with the third layer exactly above first layer.

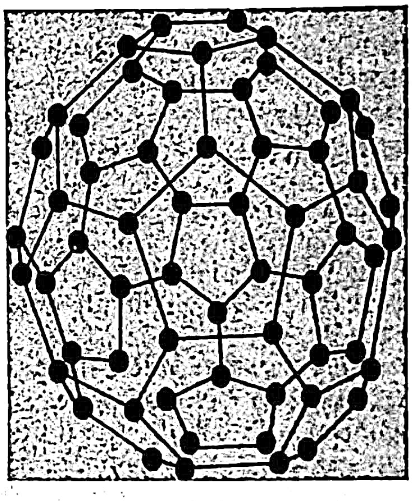
In β-graphite, the layers are arranged as ABCABC... the two forms are interconvertible.

Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less, than diamond. However entropy of graphite is more than diamond.

FULLERENE

It was made as a result of action of a laser beam or strong heating of a sample of graphite in presence of inert atmosphere. The sooty material mainly contains C_{60} with C_{70} (small amount).

Most common fullerene is C_{60} called Buckminsterfullerene which has football-like structure. It contains 20 hexagonal six-membered ring and 12 pentagonal five-membered ring. Every ring in this structure is aromatic. It is used to make ball bearings.



The structure of C_{60}, Buckminsterfullerene

Molecule of Fullerene has the shape of a soccer ball (football).

COAL

It is the crude form of carbon. It has been formed in nature as a result of slow decomposition of vegetable matter under the influence of heat, pressure and limited supply of air.

The successive stages of transformation are : peat, lignite, bituminous, steam coal and anthracite.

Bituminous is hard stone, burns with smoky flame. The superior quality is anthracite which burns with non-smoky flame.

Lamp black or carbon black: It is obtained by burning substances rich in carbon content such as kerosene, petroleum, turpentine oil, acetylene etc. in a limited supply of air.

Uses of Carbon

(*i*) **Graphite:** In making lead pencils, electrodes of electric furnances, as a moderator in nuclear reactor, as a lubricant in machinery.

(*ii*) **Charcol:** In removing offensive odour from air, in removing fused oil from crude spirit, in decolourising sugar syrup, in gas masks etc.

(*iii*) **Carbon black:** For making printing inks, black paints, Indian inks, boot polishes and ribbons of typewriters. Coal : For the manufacture of coal gas, coal tar, coke and synthetic petrol.

Train Your Brain

Example 19: Identify correct statements?

(*a*) Diamond is the hardest and graphite is the softest

(*b*) Diamond is the hardest and coke is the softest

(*c*) Diamond is the hardest and lamp black is the softest

(*d*) Coke is the hardest and diamond is the softest

Sol. (*a*) Fact based

Example 20: Different layers in graphite are held together by:

(*a*) Ionic bonding (*b*) Metallic bonding

(*c*) Covalent bonding (*d*) Vander waals forces

Sol. (*d*) Different layers in graphite are held together by Vander waals forces.

Example 21: Which of the following is a good conductor of electricity?

(*a*) Diamond (*b*) Graphite

(*c*) Coal (*d*) None

Sol. (*b*) Graphite is a good conductor of electricity

Example 22: Most stable allotrope of carbon thermodynamically is

(*a*) Fullerene (*b*) Diamond

(*c*) Graphite (*d*) Coke

Sol. (*c*) Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less, than diamond.

Example 23: Graphite conducts electricity because of the:

(*a*) highly polarized nature of π-electrons.

(*b*) highly delocalized nature of π-electrons.

(*c*) highly localized nature of π-electrons.

(*d*) None of these

Sol. (*b*) In graphite there is sp^2 hybrized carbon. thus due to highly delocalized π electrons it possess electrical conductivity.

Concept Application

20. In which of the following there exists a $p\pi - d\pi$ bonding?

(*a*) Diamond (*b*) Graphite

(*c*) Dimethylamine (*d*) Trisilylamines

21. Bucky ball or buck minster fullerene is:

(*a*) An allotrope of carbon

(*b*) It is referred as C–60

(*c*) It has sp^2-hybridised nature and its shape resembles with soccer ball

(*d*) All of these

22. Inert form of carbon is:

(*a*) Diamond (*b*) Graphite

(*c*) Coal (*d*) Charcoal

23. Consider following statements:

I: In diamond, each carbon atom is linked tetrahedrally to four other carbon atoms by sp^3 bonds.

II: Graphite has planar hexagonal layers of carbon atoms held together by weak Vander Waals forces.

III: Silicon exists only in diamond structure due to its tendency to form $p\pi - p\pi$ bonds to itself. In this:

(*a*) Only I and II are correct

(*b*) Only I is correct

(*c*) Only II and III are correct

(*d*) All are correct statement

SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

Carbon Monoxide (CO)

Structure : $:C \equiv O:$

Preparation:

(*a*) Formed due to incomplete combustion of carbon.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

(*b*) Dehydration of formic acid.

$$HCOOH \xrightarrow[\text{conc.}H_2SO_4]{373K} H_2O + CO$$

(*c*) Passing steam over coke.

$$C(s) + H_2O(g) \xrightarrow{437-1273K} \underset{\substack{\text{(Synthesis gas)} \\ \text{Water gas}}}{CO(g) + H_2(g)}$$

(*d*) Passing air over coke.

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} \underset{\text{Producer gas}}{CO(g) + 4N_2(g)}$$

CO is colourless, odourless gas and water insoluble and is a strong reducing agent.

Credit:--- Divansh.....

Carbon atom is sp hybridised. One sp orbital is being used to form a single bond with oxygen atom while the other sp orbital which points away from the C—O bond contains a lone pair of electrons the remaining two unhybridised p-orbitals form two π-bonds with two p-orbitals of oxygen atom. CO molecule acts as a donor and reacts with certain metals when heated to form metal carbonyls. It is also called **silent killer** because it maks 300 times more stable compound with haemoglobin than O_2.

(*i*) Used in extraction of Ni (**Mond's process**):

$$\underset{\text{(Impure)}}{Ni} + 4CO \xrightarrow{\Delta} [Ni(CO)_4] \xrightarrow{\Delta} \underset{\text{(pure)}}{Ni} + 4CO$$

(*ii*) It acts as a reducing agent and reduces metallic oxides to metals.

$$Fe_2O_3 + 3CO \xrightarrow{\text{High temp.}} 2Fe + 3CO_2$$

$$\underset{\text{(steam)}}{H_2O} + CO \xrightarrow{\text{High temp.}} H_2 + CO_2$$

(*iii*) CO is poisonous gas, antidote for CO poisoning is carbogen (Mixture of oxygen & 5 - 10% CO_2)

Carbon Dioxide (CO_2)

It is prepared by

(*a*) Thermal decomposition of calcium carbonate.

$CaCO_3 \rightarrow CaO + CO_2$

(*b*) Action of calcium carbonate with dil. HCl.

$CaCO_3\,(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

(*c*) Combustion of carbon containing fuels.

$$C + O_2 \xrightarrow{\Delta} CO_2$$

$$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$$

It is colourless, odourless and acidic gas as it combines with water to form carbonic acid which helps to maintain pH of blood. Plants make food from it.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{hv} C_6H_{12}O_6 + 6O_2$$

Green plants convert atmospheric CO_2 into glucose (carbohydrates) by photosynthesis.

By this process, CO_2 is reduced from atmosphere.

Unlike CO, it is not poisonous, but the increase in combustion of fossil fuels and decomposition of limestone for cement industry seem to increase the CO_2 content in atomosphere.

If CO_2 underpressure is allowed to escape through a nozzle, a white solid is obtained that is called dry ice. It can be used as refrigerant for frozen food or ice cream under the commercial name drikold.

Gaseous CO_2 is used in soft drinks It is also used as fire extinguisher as it is non-supporter of combustion and heavy. With water it gives weak dibasic acid called carbonic acid which dissociates in two steps as below

$$H_2CO_3\,(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$HCO_3^-\,(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

H_2CO_3/HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42. It combines with alkalies to form metal carbonates.

In CO_2 carbon is sp hybridised. It involves two sigma bond and two electrons of carbon contribute in pπ-pπ bonding. It is a linear molecule with carbon-oxygen double bonds. Resonance structure is as follows:

$$^-O-C\equiv O^+ \longleftrightarrow O=C=O \longleftrightarrow {}^+O\equiv C-O^-$$

It neutralises alkalies to form two series of salts, carbonates and bicarbonates.

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{(milky)}}{CaCO_3} + H_2O$$

$$\underset{\text{(milky appearance)}}{CaCO_3} + H_2O + CO_2 \longrightarrow \underset{\substack{\text{Cal. bicarbonate (clear sol.)} \\ \text{(milkiness disappear)}}}{Ca(HCO_3)_2}$$

This is used as a test of CO_2 and carbonates

Note: Carbon suboxide C_3O_2 si linear $O=C=C=C=O$

Carbides of Carbon

Compounds of C with less electronegative element are known as carbides.

A. Ionic or Salt like carbides:

Formed by ionic bonding and exists as crystalline solids.

Ionic carbide = Carbon + Highly Electropositive metal

(*a*) **Methanides:** In these, carbon is in - 4 oxidation state. When subjected for hydrolysis it form methane

$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$

(*b*) **Acetylides:** In these carbon is in -1 oxidation state. These on hydrolysis form acetylene

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

(*c*) **Allylides:** Carbon is in $-\frac{4}{3}$ oxidation state. They form propyne on hydrolysis

$Mg_2C_3 + 2H_2O \rightarrow 2Mg(OH)_2 + C_3H_4$

Note: Calcium carbide react with nitrogen to form nitrolime (Calcium cynamide). It releases NH_3 on hydrolysis so it is mainly used as fertilizer.

$CaC_2 + N_2 \rightarrow CaCN_2 + C$

$CaCN_2 + 3H_2O \rightarrow 2NH_3 + CaCO_3$

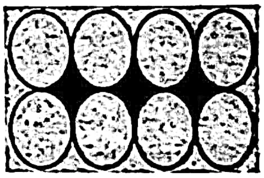
B. Covalent Carbides:

(*a*) C + Non metals = Covalent carbides (Small discrete molecules) eg : CH_4, CCl_4 etc.

(*b*) Carbides consist of giant molecules eg SiC (carborundum) etc.

These are very hard & are used for cutting

C. Interstitial carbides or Refractory Carbides:



(*i*) Interstitial sites are occupied by carbon.

(*ii*) Carbon are held by weak vander waal forces in interstitial carbides eg. Steel

(*iii*) Ti, Zr, Hg, W, Mo, V : Forms interstitial carbides, while Co, Ni, Fe do not forms interstitial carbides.

Rest of transition metal forms interstitial carbides

Credit:--- Divansh.....

(*iv*) Characteristics of interstitial compounds:

(*a*) Density is high so very hard & have high m.p. & b.p.

(*b*) They are employed in cutting of tools especially tungsten carbide.

(*v*) Interstitial compounds are non stoichiometric compounds.

Train Your Brain

Example 24: Which of the following is neutral oxide?

(*a*) CO (*b*) CO_2

(*c*) SiO_2 (*d*) NO_2

Sol. (*a*) CO_2, SiO_2, NO_2 are acidic.

Example 25: Carbon suboxide C_3O_2 has

(*a*) Linear structure

(*b*) Bent structure

(*c*) Trigonal planar structure

(*d*) Distorted tetrahedral structure

Sol. (*a*) Carbon suboxide C_3O_2 is linear $O=C=C=C=O$

Example 26: Allylides are ionic carbides. They contains :

(*a*) C^{4-} ions (*b*) C_2^{2-} ions

(*c*) C_3^{3-} ions (*d*) C_3^{4-} ions

Sol. (*d*) Allylides contain C_3^{4-} ions.

Concept Application

24. $Ca + C_2 \longrightarrow CaC_2 \xrightarrow{N_2} A$

Compound (A) is used as a/an

(*a*) Fertilizer

(*b*) Dehydrating agent

(*c*) Oxidising agent

(*d*) Reducing agent

25. Carbon reacts with metal to form:

(*a*) Carbide (*b*) Carbonate

(*c*) Hydroxide (*d*) Oxide

26. Which gas is responsible for green house effect?

(*a*) CO_2 (*b*) SO_2

(*c*) CO (*d*) SO_3

27. Which of the following statement is false?

(*a*) Dry ice is solid CO_2

(*b*) CO_2 is weakly acidic

(*c*) CO_2 and SiO_2 are linear molecules

(*d*) CO_2 is a gas while SiO_2 is solid

FUELS OF CARBON

Calorific value: It is the total quantity of heat liberated by the complete combustion of a unit mass of the fuel in air.

(*a*) **Water gas:**

(*i*) It is a mixture of $CO + H_2$ with a small amount of CO_2 & also known as synthesis gas.

(*ii*) A mixture of water gas and producer gas is used for manufacture of NH_3 by Haber's process

(*iii*) Water gas is also known as blue gas because it burns with blue flame.

(*b*) **Producer gas:**

(*i*) It is a mixture of $CO + N_2$

(*ii*) Cheapest gaseous fuel

(*c*) **Coal gas:** It is a mixture of $H_2 + CH_4 + CO$ and other gases like N_2, C_2H_4, O_2 etc.

(*d*) **Oil gas:** It is a mixture of $H_2 + CH_4 + C_2H_4 + CO$ and other gases like CO_2.

(*e*) **Gobar gas or Bio gas:** $CH_4 + CO + H_2$

(*f*) **Natural gas:** $CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}$

(*g*) **L.P.G. (Liquified Petroleum Gas):**

Butane + Isobutane

SILICON DIOXIDE

It is commonly known as silica and is nearly non-reactive because of its very high silicon-oxygen bond enthalpy. It is resistant to acids, halogens, metals and dihydrogen.

It is attacked by HF and NaOH.

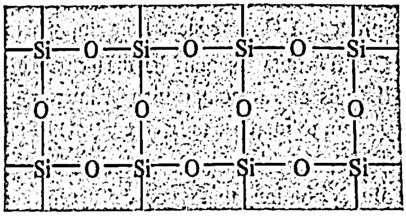
$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 2HF \rightarrow SiF_4 + 2H_2O$$

The entire solid crystal may be considered as giant molecule in which eight-membered rings are formed with alternate silicon and oxygen atoms.

Uses:

SiO_2 (silica gel) is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.



SILICONES

Alkyl chloride reacts with silicon at 537K in presence of copper catalyst to give dialkyl dichlorosilane with other substituted chlorosilane.

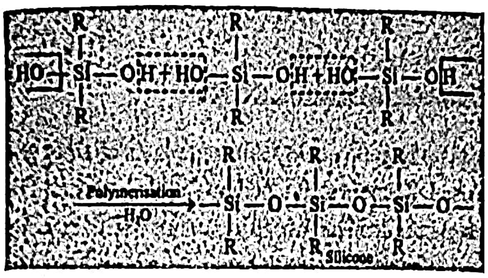
$$2RCl + Si \xrightarrow[570°C]{Cu\,powder} R_2SiCl_2$$

R_2SiCl_2 on hydrolysis gives dialkyl dihydroxy silane.

$$R_2SiCl_2 \xrightarrow[2HCl]{+2H_2O} R_2Si(OH)_2$$

$R_2Si(OH)_2$ on polymerisation gives silicones.

Credit:--- Divansh.....



Silicones are water repellants, good electrical insulators, stable towards heat, non-toxic resistant to chemicals.

These can be used in surgical and cosmetic plants. It is a polymer having $-\!\left(\overset{|}{\underset{|}{\text{Si}}}-\text{O}\right)_n\!-$ monomer. It can also be used as lubricant.

SILICATES

Oxide anion of silicon is known as silicates. There are following five types of Silicate.

(*i*) **Orthosilicates:** These do not share any corner. The anions are discrete SiO_4^{4-} units.

Examples - Zircon ($ZrSiO_4$) and Forsterite (Mg_2SiO_4).

(*ii*) **Pyrosilicate:** Here, two tetrahedral share one corner to form $Si_2O_7^{6-}$ anion. The structure posessed by them is called island structure.

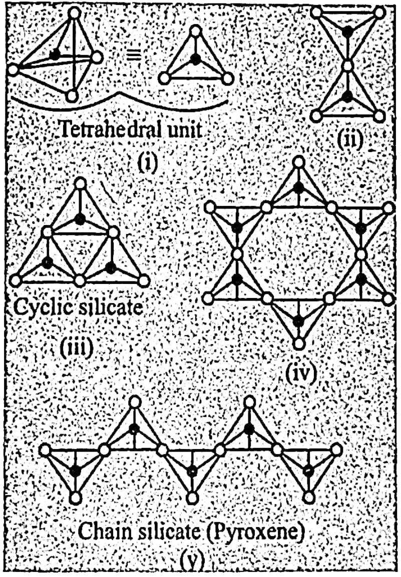
Example - Thortveitite ($Sc_2Si_2O_7$).

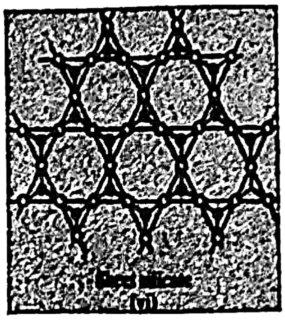
(*iii*) **Cyclic or ring silicates:** Here two corners of each tetrahedron are shared to form closed rings. The anionic unit are $(SiO_3^{2-})_n$.

Examples: Wollastonite- $Ca_3Si_3O_9$,

Beryl - $Be_3Al_2Si_6O_{18}$.

(*iv*) **Chain silicates:** Here two corners of each tetrahedron are shared to form a linear chain. The anionic unit is again $(SiO_3^{2-})_n$. Linear silicate chain is present in pyroxenes. Example - Spodumene - $LiAl(SiO_3)_2$. If two chains are cross linked, the double strand silicates $(Si_4O_{11}^{6-})_n$ are called amphiboles. Example - asbestos.





(*v*) **Sheet silicates:** These silicates are formed by the sharing of three corners of each tetrahedron. The anion has a two dimensional sheet structure with general formula $(Si_2O_5^{2-})_n$.
Example - Clay

(*vi*) **Three dimensional silicates:** These are formed by the sharing of all the four corners. Example - All the crystalline forms of silica. Example : Zeolites, Feldspar.

ZEOLITES

If Al atoms replace few silicon atoms in 3D-network of SiO_2, overall structure known as aluminosilicates acquires a negative charge.

Cations such as Na^+, K^+, Ca^{2+} etc balance the negative charge, e.g., feldspar (CaF_2) and Zeolites.

Uses

(*i*) Softening hard water by ion-exchanging.

(*ii*) Converting alcohols directly into gasoline (ZSM-5).

(*iii*) As catalyst in petrochemical industries.

GLASS

It is a transparent or translucent amorphous supercooled solid solution of silicates and borates. Its composition is variable as it is not a true compound It is also referred as pseudo solid.

Train Your Brain

Example 27: In silicon dioxide:

(*a*) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.

(*b*) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms.

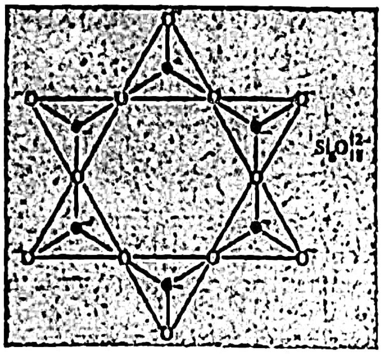
(*c*) Silicon atom is bonded to two oxygen atoms

(*d*) There are double bonds between silicon and oxygen atoms.

Sol. (*a*) Each Si atom is surrounded by four O atoms and each oxygen atom is bonded to two Si atoms.

Example 28: Draw the structure of cyclic silicate containing $Si_6O_{18}^{12-}$ ion.

Sol.

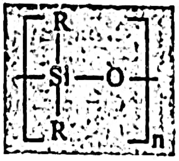


Example 29: $RCl \xrightarrow[Si]{Cu\text{-powder}} R_2SiCl_2 \xrightarrow{H_2O} R_2Si(OH)_2 \xrightarrow{condensation}$ A. Here Compound (A) is:

(*a*) A linear silicone (*b*) A chlorosilane

(*c*) A linear silane (*d*) A network silane

Sol. (*a*) It form linear silicon



$$\left[-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-\right]_n$$

Concept Application

28. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be:

(*a*) Sodium

(*b*) Magnesium

(*c*) Mercury

(*d*) Tin

29. Lead pipes are readily corroded by:

(*a*) Dil. H_2SO_4 (*b*) Conc. H_2SO_4

(*c*) Acetic acid (*d*) Water

30. Silicone resins are made by:

(*a*) Dissolving a mixture of $PhSiCl_3$ and $(Ph)_2SiCl_2$ in toluene and then hydrolysing with water.

(*b*) Hydrolysing a mixture of $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$.

(*c*) Hydrolysis of $(CH_3)_2SiCl_2$

(*d*) None of these

MINDFUL ART CREATION

- Paint, draw, or create something for someone else with full focus on the process. Let your art express gratitude or positive emotions.
- Gift your creation as a token of kindness, channeling mindfulness into creative expression while spreading positivity.

Aarambh (Solved Examples)

1. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

Sol. Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

2. Boron is unable to form BF_6^{3-} ion. Explain.

Sol. Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalency of boron cannot exceed 4.

3. Why is boric acid considered as a weak acid?

Sol. Because it is not able to release H^+ ions on its own. It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.

4. Select the member(s) of group 14 that (*i*) forms the most acidic dioxide, (*ii*) is commonly found in +2 oxidation state, (*iii*) is used as semiconductor.

Sol. (*i*) Carbon

(*ii*) Lead

(*iii*) Silicon and germanium

5. Diamond is covalent, yet it has high melting point. Why?

Sol. Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

6. SiH_4 is more reactive than CH_4. Explain why.

Sol. The main reasons are:

(*i*) Silicon is having vacant d orbital which is not in case of carbon.

(*ii*) Silicon is larger in size compared to C. Hence the incoming Nu– doesn't face any steric hindrance to attack at Si whereas CH_4 is tightly held from all sides.

7. Regular use of which of the following fertilizer increases the acidity of soil:

(*a*) Potassium nitrate

(*b*) Urea

(*c*) Superphosphate of lime

(*d*) Ammonium sulphate

Sol. Regular use of ammonium sulphate increases the acidity of soil. The hydrolysis of ammonium sulphate produces sulphuric acid which increases the acidity of soil.

$$(NH_4)_2SO_4 + 2H_2O \rightarrow 2NH_3 + 2H_2O + H_2SO_4$$

To prevent acidity, slaked lime is added to neutralize the acid.

Therefore, option (*d*) is the correct answer.

8. The hydrolysis of alkyl substituted chlorosilanes give—

Sol. Silicones

$$R_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} R_2Si(OH)_2$$

$$nR_2Si(OH)_2 \xrightarrow{-(n-1)H_2O} (R_2SiO)_n \text{ silicone}$$

9. Boron form covalent compound due to

(*a*) Higher ionization energy

(*b*) Lower ionization energy

(*c*) Small size

(*d*) Both (*a*) and (*c*)

Sol. Due to small size and higher ionization energy, boron form covalent compound.

Therefore, option (*d*) is the correct answer.

10. Aluminium is more reactive than iron. But aluminium is less easily corroded than iron because:

(*a*) Formation of a protective oxide layer on aluminium

(*b*) Aluminium is a noble metal

(*c*) Iron easily undergoes reaction with water

(*d*) Iron forms mono and divalent ions

Sol. Due to formation of a protective oxide layer of Al_2O_3 on aluminium.

Therefore, option (*a*) is the correct answer.

11. The hydrides of boron are called

(*a*) Boron hydrogen compounds

(*b*) Hydrogen borides

(*c*) Boranes

(*d*) Hydroboric acids

Sol. The hydrides of boron are known as boranes.

Therefore, option (*c*) is the correct answer.

12. Which one of the following does not exist in the free form?

(*a*) BF_3 (*b*) BCl_3

(*c*) BBr_3 (*d*) BH_3

Sol. BH_3 exist as a dimeric form (B_2H_6).

Therefore, option (*d*) is the correct answer.

13. Which of the following is most acidic?

(*a*) Na_2O (*b*) MgO

(*c*) Al_2O_3 (*d*) CaO

Sol. Na_2O, MgO, CaO are basic in nature while Al_2O_3 is amphoteric in nature.

Therefore, option (*c*) is the correct answer.

14. The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ mol^{-1}) of C—C, Si—Si and Ge—Ge bonds are respectively:

(*a*) 348, 260, 297 (*b*) 348, 297, 260

(*c*) 297, 348, 260 (*d*) 260, 297, 348

Sol. Ge has lowest bond energy, hence lowest catenation tendency. C has highest bond energy, hence highest catenation tendency.

Therefore, option (*b*) is the correct answer.

15. On heating oxalic acid with H_2SO_4, we get

(*a*) H_2CO_3

(*b*) CO_2 and O_2

(*c*) CO_2 and CO

(*d*) $H_2CO_3 + CO_2 + O_2$

Sol. $H_2C_2O_4 \xrightarrow{H_2SO_4} H_2O + CO + CO_2$

Therefore, option (*c*) is the correct answer.

16. In what respect, the reaction of N_2 with (*i*) CaC_2 (calcium carbide) (*ii*) BaC_2 (barium carbide) differ from each other?

Sol. (*i*) CaC_2 reacts with N_2 to form calcium cyanamide.

$$CaC_2(s) + N_2(g) \xrightarrow{1373K} \underset{\text{Calcium cyanamide}}{CaCN_2(s)} + C(s)$$

(*ii*) BaC_2 reacts with N_2 to form barium cyanide

$$BaC_2(s) + N_2(g) \xrightarrow{\text{Heating}} \underset{\text{Barium cyanide}}{Ba(CN)_2\ (s)}$$

17. Complete the following reactions

(*a*) $CO + H_2 \xrightarrow[420-670k,\ 300atm]{ZnO+Cu}$ ....

(*b*) $R_3SiOH + OHSiR_3 \longrightarrow$ .... + ...

(*c*) $Na_2CO_3 + Si \longrightarrow$ .... + ...

Sol. (*a*) $CO + 2H_2 \xrightarrow[420-670k,300atm]{ZnO+Cu} CH_3OH$

(*b*) $R_3SiOH + OHSiR_3 \longrightarrow R_3Si{-}O-SiR_3 + H_2O$

(*c*) $Na_2CO_3 + Si \longrightarrow Na_2SiO_3 + C$

DIGITAL DETOX AND GRATITUDE

- Take a day off from social media and devices to connect with the people around you or journal about the things you're grateful for.
- Reflect on how this detox enhances your mindfulness by reducing distractions and increasing self-awareness and appreciation for the present moment.

School Level Problems

SINGLE CORRECT TYPE QUESTIONS

1. Which of the following is least stable compound?

   (*a*) BCl_3 (*b*) $GaCl_3$

   (*c*) $InCl_3$ (*d*) $TlCl_3$

2. The outer electronic configuration of group-13 elements is:

   (*a*) $ns^2 np^2$ (*b*) $ns^2 np^6$

   (*c*) $ns^2 np^1$ (*d*) $ns^2 np^4$

3. Which of the following statement is incorrect about boron?

   (*a*) It is metallic in nature

   (*b*) It is extremely hard and black coloured solid

   (*c*) It has unusually high melting point

   (*d*) It exists in many allotropic forms

4. Aluminium and gallium oxides are

   (*a*) Acidic (*b*) Basic

   (*c*) Amphoteric (*d*) None of these

5. Which element is used in making transistor?

   (*a*) Sn (*b*) Sb

   (*c*) Si (*d*) Mg

6. Which of the following oxidation states are the most characteristic for lead and tin respectively?

   (*a*) +2, +2 (*b*) +4, +2

   (*c*) +2, +4 (*d*) +4, +4

7. The hybridization state of carbon in fullerene is:

   (*a*) sp (*b*) sp^2

   (*c*) sp^3 (*d*) sp^3d

8. The ratio of "Si" and "O" atoms in silica is:

   (*a*) 1 : 2 (*b*) 2 : 1

   (*c*) 1 : 4 (*d*) 4 : 1

ASSERTION AND REASON TYPE QUESTIONS

Directions(Q. 9 to 10): These questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(*a*) Both Assertion (A) and Reason (R) are True and the Reason (R) is a correct explanation of the Assertion (A).

(*b*) Both Assertion (A) and Reason (R) are True but Reason (R) is not a correct explanation of the Assertion (A).

(*c*) Assertion (A) is True but the Reason (R) is False.

(*d*) Assertion (A) is False but Reason (R) is True.

9. **Assertion (A):** Silicones are water repelling in nature.

   Reason (R): Silicones are organosilicon polymers, which have $(-R_2SiO-)$ as repeating unit.

10. **Assertion (A):** Pb^{4+} can be reduced easily to Pb^{2+}.

    Reason (R): The stability of lower oxidation state is due to inert pair effect.

MATCH THE COLUMN TYPE QUESTIONS

11. Match the species given in Column-I with properties given in Column-II.

	Column-I		Column-II
A.	Diborane	(p)	Used as a flux for soldering metals
B.	Gallium	(q)	Crystalline form of silica
C.	Borax	(r)	Banana bonds
D.	Aluminosilicate	(s)	Low melting, high boiling, useful for measuring high temperatures
E.	Quartz	(t)	Used as catalyst in petrochemical industries

(*a*) A-(q), B-(p), C-(r), D-(s), E-(t)

(*b*) A-(t), B-(q), C-(r), D-(p), E-(s)

(*c*) A-(q), B-(p), C-(s), D-(t), E-(r)

(*d*) A-(r), B-(s), C-(p), D-(t), E-(q)

12. Match the species given in Column-I with the properties mentioned in Column II.

	Column-I		Column-II
A.	BF_4^-	(p)	Oxidation state of central atom is +4
B.	$AlCl_3$	(q)	Strong oxidising agent
C.	SnO	(r)	Lewis acid
D.	PbO_2	(s)	Can be further oxidised
		(t)	Tetrahedral shape

(*a*) A-(s), B-(s), C-(p), D-(q), E-(t)

(*b*) A-(t), B-(r), C-(s), D-(p,q), E-(s)

(*c*) A-(p), B-(q), C-(t), D-(r), E-(p)

(*d*) A-(q), B-(p), C-(s), D-(q), E-(s)

SHORT ANSWER TYPE QUESTIONS

13. Describe the preparation methods for carbon monoxide (CO) and discuss the industrial applications of water gas and producer gas as fuels, highlighting their combustion processes?

14. Describe the structure and properties of diborane (B_2H_6), and explain its significance in organic synthesis and as a reducing agent?

15. Explain the interaction of BCl_3 and CCl_4 with water, and provide a justification for their differing behaviors based on their chemical properties and structures?

16. Explain the electron-deficient nature of BCl_3 and $SiCl_4$, and elucidate the criteria that classify them as Lewis acids, considering the electron configuration and bonding characteristics of their central atoms?

17. What are the properties and applications of graphite as a carbon allotrope? Highlight its distinctive structural characteristics and their roles in enabling electrical conductivity and lubrication properties.

18. Explain the mechanism by which excess carbon dioxide (CO_2) contributes to global warming, including how CO_2 absorbs heat radiated by the Earth and its impact on the Earth's temperature?

LONG ANSWER TYPE QUESTIONS

19. Describe the properties and reactions of borax (sodium borate), including its chemical formula and its behavior when dissolved in water. Explain the transformation of borax upon heating and how it is utilized in the borax bead test to identify transition metals, using the example of CoO.

20. Explain the properties, preparation, and reactivity of orthoboric acid (H_3BO_3). Describe its structural arrangement involving BO_3 units and its role as a Lewis acid. Also, briefly outline the thermal decomposition of orthoboric acid, leading to metaboric acid and boric oxide formation.

21. Provide a comprehensive overview of carbon allotropes, with a specific focus on diamond. Explain the crystal structure, properties, and characteristics that differentiate diamond from other carbon allotropes. Highlight its significance in various industries and applications.

22. Why does aluminum trifluoride show insolubility in anhydrous HF but become soluble upon the addition of NaF? Furthermore, explain the phenomenon that causes aluminium trifluoride to precipitate when gaseous BF_3 is introduced into the resulting solution?

23. Explain the structural unit of silicates, SiO_4^{4-}, and how they combine to form various structures like chains, rings, sheets, or three-dimensional networks. Describe how metal ions neutralize the negative charge in silicate structures. Provide industrial examples of man-made silicates and discuss the role of aluminosilicates, particularly zeolites, in catalysis and ion exchange?

CASE STUDY BASED QUESTIONS

24. Group 13 and Group 14 elements play pivotal roles in various aspects of our lives. Group 13 includes elements like boron, aluminium, and gallium, known for their unique properties and applications. Boron, for instance, is utilized in the production of borosilicate glass, a heat-resistant and durable material used in laboratory equipment and cookware. Aluminium, on the other hand, is a lightweight metal widely employed in the aerospace industry for its exceptional strength-to-weight ratio.

Group 14 elements consist of carbon, silicon, germanium, tin, and lead. Carbon, in the form of graphite and diamond, showcases remarkable differences in properties due to its allotropes. Silicon is the foundation of modern electronics, serving as the basis for semiconductors and integrated circuits. Germanium was historically used in early transistors, while tin is employed in various alloys, including pewter. Lead, though once commonly used, is now recognized for its toxicity and phased out in many applications.

These elements contribute to the advancement of technology, industry, and health. Understanding their properties and applications is essential for harnessing their potential effectively.

(i) Which Group 13 element finds application in the production of borosilicate glass, and what are the key properties that make borosilicate glass desirable in laboratory and kitchenware?

(*a*) Aluminium (*b*) Boron
(*c*) Gallium (*d*) Silicon

(ii) What is the primary role of silicon, a Group 14 element, in the field of electronics, and why is it crucial for the development of integrated circuits and semiconductors?

(*a*) Silicon is a key component in solar panels.
(*b*) Silicon is used in the production of batteries.
(*c*) Silicon is essential for making magnetic materials.
(*d*) Silicon is the main material for integrated circuits.

(iii) Among Group 14 elements, which one has been historically used in early transistors due to its semiconducting properties?

(*a*) Carbon (*b*) Tin
(*c*) Germanium (*d*) Lead

(iv) What is the current status of the use of lead, a Group 14 element, in various applications, and why has it been phased out in many cases?

(*a*) Lead is still widely used in plumbing systems.
(*b*) Lead is phased out due to its toxicity and health risks.
(*c*) Lead is primarily used [illegible] aerospace industry.
(*d*) Lead is essential in th [illegible] of modern electronics.

Credit:--- Divansh.....

BORON AND ITS PROPERTIES

1. TlI_3 is an ionic compound which furnishes the following ions in solution:
   (a) Tl^{3+} and I^- ions
   (b) Tl^+ and I_3^- ions
   (c) Tl^+, I^- ions and I_2
   (d) Tl^+ and I^- ions
2. Which is true for an element R present in group 13 of the periodic table?
   (a) It is gas at room temperature
   (b) It has oxidation state of +4
   (c) It forms R_2O_3
   (d) It forms RX_2
3. In diborane
   (a) 4 bridged hydrogens and two terminal hydrogen are present
   (b) 2 bridged hydrogens and four terminal hydrogen are present
   (c) 3 bridged and three terminal hydrogen are present
   (d) None of the above
4. A mixture of boric acid with ethyl alcohol burns with green edged flame due to the formation of
   (a) Ethyl borax (b) Ethyl borate
   (c) Methyl borax (d) Methyl borate
5. Which of the following is known as inorganic benzene?
   (a) Borazine (b) Boron nitride
   (c) p-dichlorobenzene (d) Phosphonitrilic acid
6. BCl_3 does not exist as dimer but BH_3 exist as dimer (B_2H_6) because
   (a) Chlorine is more electronegative than hydrogen
   (b) There is pπ-pπ back bonding in BCl_3 but BH_3 does not contain such multiple bonding
   (c) Large sized chlorine atoms do not fit in between the small boron atoms whereas small sized hydrogen atoms get fitted in between boron atoms
   (d) None of the above
7. Which of the following is the electron deficient molecule?
   (a) B_2H_6 (b) C_2H_6
   (c) PH_3 (d) SiH_4
8. Acidic strength of Boron trihalide are in order of
   (a) $BF_3 < BCl_3 < BBr_3 < BI_3$
   (b) $BI_3 < BBr_3 < BCl_3 < BF_3$
   (c) $BBr_3 < BCl_3 < BF_3 < BI_3$
   (d) $BF_3 < BI_3 < BCl_3 < BBr_3$

PROPERTIES OF ALUMINIUM AND ITS COMPOUNDS

9. Aluminium is a self-preserving metal, because
   (a) It is not tarnished by air
   (b) of formation of a thin film of basic carbonate on its surface
   (c) of formation of a non-porous layer of oxide is formed on its surface
   (d) It is not affected by salt water
10. In the thermite process the reducing agent is
   (a) Al (b) C (c) Mg (d) Na
11. Alum is found to contain hydrated monovalent cation $[M(H_2O)_6]^+$, trivalent cation $[M'(H_2O)_6]^{+3}$ and SO_4^{2-} in the ratio of:
   (a) 1 : 1 : 1 (b) 1 : 1 : 2 (c) 1 : 2 : 2 (d) 1 : 2 : 3
12. Aluminium hydroxide is soluble in excess of sodium hydroxide forming the ion
   (a) AlO_2^{+3} (b) AlO_2^{-3} (c) AlO_2^- (d) AlO_3^-
13. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives
   (a) $[Al(OH)_6]^{3-} + 3HCl$ (b) $[Al(H_2O)_6]^{3+} + 3Cl^-$
   (c) $Al^{3+} + 3Cl^-$ (d) $Al_2O_3 + 6HCl$
14. Aluminium vessels should not be washed with materials containing washing soda since
   (a) Washing soda is expensive
   (b) Washing soda is easily decompose
   (c) Washing soda reacts with aluminium to form soluble aluminate
   (d) Washing soda reacts with aluminium to form insoluble aluminium oxide
15. Aluminium (III) chloride forms a dimer because
   (a) Higher coordination number can be achieved by aluminium
   (b) Aluminium has high ionization energy
   (c) Aluminium belongs to III group
   (d) It cannot form a trimer

GENERAL CHARACTERISTIC OF C-FAMILY AND ITS COMPOUNDS

16. Amongst the elements of group 14, the reducing power of the divalent species decreases in the order
   (a) Ge > Sn > Pb (b) Sn > Ge > Pb
   (c) Pb > Sn > Ge (d) Sn > Pb > Ge

Credit:--- Divansh.....

17. Carbon-60 contains:
(*a*) 20 pentagons and 12 hexagons
(*b*) 12 pentagons and 20 hexagons
(*c*) 30 pentagons and 30 hexagons
(*d*) 24 pentagons and 36 hexagons

18. Suppose you have to determine the percentage of carbon dioxide in a sample of a gas available in a container. Which is the best material for adsorption of the carbon dioxide?
(*a*) Heated copper oxide
(*b*) Cold, solid calcium chloride
(*c*) Cold, solid calcium hydroxide
(*d*) Heated charcoal

19. Which is used to produce smoke screens?
(*a*) Calcium phosphide
(*b*) Zinc sulphide
(*c*) Sodium carbonate
(*d*) Zinc phosphide

20. Silicones have the general formula
(*a*) SiO_4^{4-}
(*b*) $Si_2O_7^{6-}$
(*c*) $(R_2SiO)_n$
(*d*) $(SiO_3)_n^{2-}$

21. Which of the following attacks glass?
(*a*) HCl
(*b*) HF
(*c*) HI
(*d*) HBr

22. Lead pipes are not suitable for drinking water because
(*a*) A layer of lead dioxide is deposited over pipes
(*b*) Lead reacts with air to form litharge
(*c*) Lead reacts with water containing air to form $Pb(OH)_2$
(*d*) Lead forms basic lead carbonate

23. H_2O_2 on reaction with PbS gives
(*a*) PbO (*b*) $PbSO_4$ (*c*) PbO_2 (*d*) $PbHSO_4$

24. Which of the following is a mixed oxide?
(*a*) Fe_2O_3 (*b*) PbO_2 (*c*) Pb_3O_4 (*d*) BaO_2

25. When tin is treated with concentrated nitric acid
(*a*) It is converted into stannous nitrate
(*b*) It is converted into stannic nitrate
(*c*) It is converted into metastannic acid
(*d*) It becomes passive

26. White lead is
(*a*) $PbCO_3$
(*b*) $PbCO_3.PbO$
(*c*) $2PbCO_3.Pb(OH)_2$
(*d*) $2PbSO_4.PbO$

27. Litharge is chemically
(*a*) PbO
(*b*) PbO_2
(*c*) Pb_3O_4
(*d*) $Pb(CH_3COO)_2$

28. Percentage of lead in lead pencil is
(*a*) Zero (*b*) 20 (*c*) 80 (*d*) 70

29. Which of the following lead oxides is 'Sindhur'?
(*a*) PbO (*b*) PbO_2 (*c*) Pb_2O_3 (*d*) Pb_3O_4

Prabal (JEE Main Level)

1. The decrease in stability of higher oxidation state in p-block with increasing atomic number is due to:
(*a*) Increase in bond energy going down the group.
(*b*) The reluctance of s-subshell electrons to participate in the chemical bonding.
(*c*) Both are correct.
(*d*) None is correct.

2. Crystalline boron in small amounts may be obtained by:
(*a*) Reducing BCl_3 with H_2
(*b*) Pyrolysis of BI_3
(*c*) Thermal decomposition of diborane
(*d*) All of these

3. Borax is:
(*a*) $Na_2B_4O_7$
(*b*) $Na_2B_4O_7.4H_2O$
(*c*) $Na_2B_4O_7.7H_2O$
(*d*) $Na_2B_4O_7.10H_2O$

4. $H_3BO_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{red hot}} B_2O_3$
it $T_1 < T_2$ then X and Y respectively are
(*a*) X = Metaboric acid and Y = Tetraboric acid
(*b*) X = Tetraboric acid and Y = Metaboric acid
(*c*) X = Borax and Y = Metaboric acid
(*d*) X = Tetraboric acid and Y = Borax

5. Borax bead test is responded by:
(*a*) divalent metals
(*b*) Heavy metals
(*c*) Light metals
(*d*) Metal which forms coloured metaborates

6. H_2S gas can be obtained by the action of water on:
(*a*) CuS
(*b*) FeS
(*c*) Flower of sulphur
(*d*) Al_2S_3

7. Which of the following is only acidic in nature?
(*a*) $Be(OH)_2$
(*b*) $Mg(OH)_2$
(*c*) $B(OH)_3$
(*d*) $Al(OH)_3$

8. Aluminium becomes passive towards
(*a*) NaOH
(*b*) conc. HCl
(*c*) N_2
(*d*) conc. HNO_3

9. Aqueous solution of potash alum is:
(*a*) alkaline
(*b*) Acidic
(*c*) Neutral
(*d*) Soapy

Credit:--- Divansh.....

10. Which mixed sulphate is not an alum?

(*a*) $K_2SO_4.Al_2(SO_4)_3.24H_2O$

(*b*) $K_2SO_4.Cr_2(SO_4)_3.24H_2O$

(*c*) $Na_2SO_4.Fe_2(SO_4)_3.24H_2O$

(*d*) $CuSO_4.Al_2(SO_4)_3.24H_2O$

11. An aqueous solution of BCl_3 is:

(*a*) Weak acid (*b*) Weak base

(*c*) Neutral (*d*) Strong base

12. Elements of group 14:

(*a*) Exhibit oxidation state of +4 only

(*b*) Exhibit oxidation state of +2 and +4

(*c*) Form M^{-2} and M^{4+} ions

(*d*) Form M^{2+} and M^{4+} ions

13. Methanides are:

(*a*) Mg_2C_3, Be_2C, Al_4C_3 and CaC_2

(*b*) Mg_2C_3, Be_2C and Al_4C_3

(*c*) Be_2C, Al_4C_3 and CaC_2

(*d*) Be_2C and Al_4C_3

14. When oxalic acid reacts with conc. H_2SO_4, two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively____

(*a*) K_2CO_3 and CO_2 (*b*) $KHCO_3$ and CO_2

(*c*) K_2CO_3 and CO (*d*) $KHCO_3$ and CO

15. Coal gas is a mixture of:

(*a*) CO and H_2

(*b*) H_2, CH_4 and CO,

(*c*) saturated and unsaturated hydrocabons

(*d*) CO, CO_2 and CH_4

16. The ions present in Al_4C_3, CaC_2 and Mg_2C_3 are respectively:

(*a*) $C^{4-}, C_2^{2-}, C_3^{4-}$ (*b*) $C_2^{2-}, C^{4-}, C_3^{4-}$

(*c*) $C_3^{4-}, C_3^{2-}, C^{4-}$ (*d*) $C_3^{4-}, C^{4-}, C_2^{2-}$

17. Select incorrect statement:

(*a*) Interstitial carbides are formed by metalloids like Si and B

(*b*) SiC is called carborundum

(*c*) CO and CN^- both are fatal due to complex formation with Fe(III) present in blood

(*d*) CO is obtained as by-product when carbon and SiO_2 is used in reduction processes of phosphate rock to give phosphorus.

18. The hydroxide of which metal ion is soluble in excess of sodium hydroxide solution?

(*a*) Fe^{3+} (*b*) Cr^{3+}

(*c*) Sn^{2+} (*d*) Cu^{2+}

19. Unlike $PbCl_4$, PbI_4 and $PbBr_4$ are not found because:

(*a*) Bromine and iodine are more electronegative than chlorine.

(*b*) Iodine and bromine are smaller in size.

(*c*) Larger iodide and bromide ions are able to reduce Pb^{4+} to Pb^{2+} or Pb.

(*d*) The statement is incorrect.

20. Which of the following halides is least stable and has doubtful existence?

(*a*) CI_4 (*b*) GeI_4

(*c*) SnI_4 (*d*) PbI_4

21. Which of the following does not exist?

(*a*) $Si(OH)_4$ (*b*) $B(OH)_4^-$

(*c*) $SiCl_6^{2-}$ (*d*) AlF_6^{3-}

22. Which of the following statement is incorrect regarding the substance known as Plumbago or black lead?

(*a*) It is good conductor of electricity

(*b*) It's formula is $PbO \cdot 2PbO_2$

(*c*) It leaves black mark on paper

(*d*) It is very soft and slippery

23. The Soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons get converted to grey powder. This transformation is related to:

(*a*) An interaction with water vapour contained in humid air

(*b*) A change in crystalline structure of tin

(*c*) A change in the partial pressure of O_2 in air

(*d*) An interaction with N_2 of air at low temperature

24. Which of the following is not produced when mixture of borax and $CuSO_4$ is heated at high temperature?

(*a*) $Cu(BO_2)_2$ (*b*) $NaBO_2$

(*c*) B_2O_3 (*d*) Na_3BO_3

25. Alumina is insoluble in water because:

(*a*) It is a covalent compound

(*b*) It has high lattice energy and low heat of hydration

(*c*) It has low lattice energy and high heat of hydration

(*d*) Al^{3+} and O^{2-} ions are not excessively hydrated

26. Colour of the bead in borax bead test is mainly due to the formation of

(*a*) Metal oxides

(*b*) Boron oxide

(*c*) Metal metaborates

(*d*) Elemental boron

27. Which of the following is sparingly soluble in cold water and fairly soluble in hot water?

(*a*) $Pb(NO_3)_2$ (*b*) $PbCl_2$

(*c*) $PbSO_4$ (*d*) $PbCrO_4$

28. Carborundum is a:

(*a*) Molecular solid (*b*) Covalent solid

(*c*) Ionic solid (*d*) Amorphous solid

Credit:--- Divansh.....

29. The plague of tin is the:

(*a*) Conversion of stannous to stannic

(*b*) Conversion to white tin to grey tin

(*c*) Emission of sound while bending a tin rod

(*d*) Atmospheric oxidation of tin

30. The butter of tin is represent by:

(*a*) $SnCl_2 \cdot 5H_2O$ (*b*) $SnCl_2$

(*c*) $SnCl_4$ (*d*) $SnCl_4 \cdot 5H_2O$

31. Borax in its crystal possess:

(*a*) 3 tetrahedral unit

(*b*) 2 tetrahedral and 2 planar triangular units

(*c*) 3 tetrahedral and 2 planar triangular units

(*d*) All tetrahedral units

32. (*a*) Al $\xrightarrow{N_2}$ A; (*b*) Al $\xrightarrow{C}$ B.

Product A and B on hydrolysis yields respectively.

(*a*) Ammonia and acetylene

(*b*) Ammonia and methane

(*c*) Nitric oxide and acetylene

(*d*) None of the above

INTEGER TYPE QUESTIONS

33. Find the maximum number of atoms lying in the same plane for B_2H_6.

34. 1 mole of B_2H_6 (g) on hydrolysis yields .... moles of H_2(g).

35. How many of the following oxides are **amphoteric** in nature?

PbO, PbO_2, SnO, SnO_2, Al_2O_3, ZnO, BeO, CaO, B_2O_3

36. $Mg + B \longrightarrow Mg_xB_y \xrightarrow{HCl}$ Diborane

Report your answer as (x + y).

37. How many of the following substance are **having higher** lattice energy than NaBr?

$CaCl_2$, NaI, CsBr, LiF, MgO, Al_2O_3, TiO_2

38. How many of the following statements are correct regarding allotropes of carbon:

(*a*) Graphite is not a good conductor of electricity in perpendicular direction of layers at ordinary temperatures.

(*b*) Coke is the impure form of carbon.

(*c*) Anthracite is the purest form of Carbon.

(*d*) Buckminister fullerene contains 12 five membered rings and 20 six-membered rings.

(*e*) Diamond is a good conductor of Heat.

(*f*) Graphite is diamagnetic in nature.

(*g*) Graphite is thermodynamically more stable than diamond

39. Find total number of Boron atoms in anionic part of borax which participate in back bonding.

40. Find total number of moles of hydrochloric acid reacting with one mole of borax to converts all borons to boric acid:

Parikshit (JEE Advanced Level)

SINGLE CORRECT TYPE QUESTIONS

1. Artificial gem used for cutting glass is:

(*a*) Graphite (*b*) Diamond

(*c*) SiC (*d*) $CaCN_2$

2. Which of the following properties describes the diagonal relationship between boron and silicon?

(*a*) BCl_3 is not hydrolysed while $SiCl_4$ can be hydrolysed.

(*b*) Both form oxides; B_2O_3 is amphoteric; SiO_2 is acidic.

(*c*) Both metals dissolve in cold and dilute nitric acid.

(*d*) Borides and silicides are hydrolysed by water.

3. Borax is actually made of two tetrahedra and two triangular units joined together and should be written as: $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

Consider the following statements about borax:

(P) Each boron atom has four B—O bonds.

(Q) Each boron atom has three B—O bonds.

(R) Two boron atoms have four B—O bonds while other two have three B—O bonds.

(S) Each boron atom has one —OH groups.

Select correct statements:

(*a*) P and Q (*b*) Q and R (*c*) R and S (*d*) P and R

4. Aluminium is more reactive than iron because its standard reduction potential is high still aluminium is less easily corroded than iron because:

(*a*) It has higher reducing power and forms self protective layer of Al_2O_3

(*b*) It has higher reducing power and does not react with oxygen so easily

(*c*) Al reacts with atmospheric carbon dioxide to form a self protective layer of $Al_2O_3 + Al_4C_3$.

(*d*) All of the above

5. Consider the following statements for diborane:

1. Boron is approximately sp^3 hybridized
2. B-H-B angle is 180°
3. There are two terminal B-H bonds for each boron atom
4. There are only 12 bonding electrons available of these statements:

(*a*) 1, 3 and 4 are correct (*b*) 1, 2 and 3 are correct

(*c*) 2, 3 and 4 are correct (*d*) 1, 2 and 4 are correct

6. Consider the following statements and which of the following are correct?

S_1: $B_4O_7^{2-}$ on hydrolysis with acid / water yields $B(OH)_3$

S_2: SiO_4^{4-} on hydrolysis with acid / water yields $Si_2O_7^{6-}$

S_3: $MeSiCl_3$ on hydrolysis and then condensations gives a complex cross-linked polymer of silicones.

S_4: Among CO_2, CuO, CaO and H_2O, CO_2 is most acidic oxide while CaO is most basic oxide.

(*a*) S_1, S_2, S_3 only
(*b*) S_1, S_3, S_4 only
(*c*) S_1, S_2, S_3 and S_4
(*d*) S_2, S_3, S_4 only

7. A complex cross-linked polymer (silicone) is formed by

(*a*) Hydrolysis of $(CH_3)_3$ SiCl.
(*b*) Hydrolysis of a mixture of $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$
(*c*) Hydrolysis of CH_3SiCl_3
(*d*) Hydrolysis of $SiCl_4$.

8. Borax is converted into crystalline boron by the following steps:

$$\text{Borax} \xrightarrow{X} H_3BO_3 \xrightarrow{\Delta} B_2O_3 \xrightarrow[\Delta]{Y} B$$

X and Y are respectively

(*a*) HCl, Mg
(*b*) HCl, C
(*c*) C, Al
(*d*) HCl, Al

9. Which of the following statements is correct regard the C–O bond of a CO molecule upon the bond formation between BH_3 and CO?

(*a*) It gets longer because there will be π-back donation from BH_3 to CO.
(*b*) It gets longer because CO donates π-bonding electrons to BH_3.
(*c*) No or slight change on it because CO donates its mainly non-bonding electrons to BH_3.
(*d*) It gets shorter because CO donates π* anti-bonding electrons to BH_3.

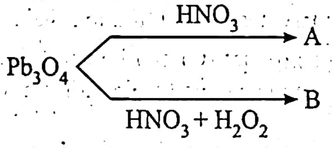
10. Reaction of ammonia with diborane gives an ionic product ($B_2H_6.2NH_3$). The hybridization of boron in the cation and anion of this product are respectively

(*a*) sp^3 in both
(*b*) sp^3 and sp^2
(*c*) sp^2 & sp^3
(*d*) sp^2 in both

11. Which of the following has the minimum heat of dissociation?

(*a*) $[(CH_3)_3N \rightarrow BF_3]$
(*b*) $[(CH_3)_3N \rightarrow B(CH_3)F_2]$
(*c*) $[(CH_3)_3N \rightarrow B(CH_3)_2F]$
(*d*) $[(CH_3)_3N \rightarrow B(CH_3)_3]$

12. In the following reactions, the Pb compounds A and B are respectively

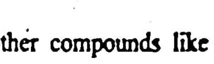


(*a*) $Pb(NO_3)_2 + PbO_2$ and $Pb(NO_3)_2$
(*b*) $Pb(NO_3)_2$ and $Pb(NO_3)_2$
(*c*) PbO_2 and $Pb(NO_3)_2$
(*d*) $Pb(NO_3)_2$ and $PbO_2 + Pb(NO_3)_2$

13. Which of the following occurs as a consequence of inert pair effect?

A. $SnCl_2$ act as a reducing agent.
B. $SnCl_4$ act as an oxidizing agent
C. SnO_2 is amphoteric
D. PbO_2 is an oxidant
E. CCl_2 is unstable but $PbCl_2$ is stable

(*a*) A, D, E
(*b*) D, E
(*c*) A, B, C, D, E
(*d*) A, B, C

14. O=Si=O structure of silica is not correctly represented but some other compounds like  have significant π-character between Si and O. It is mainly due to:

(*a*) silica have 3-D network like structure.
(*b*) in silica Si is central atom but in $(SiH_3)_2O$, O is central atom.
(*c*) with respect to orbitals, π-bond is different in origin in both case.
(*d*) in SiO_2 covalent type π-bond formation is required but in $(SiH_3)_2O$ co-ordinate type π-bond formation is required.

15. Select INCORRECT option for $(Si_4O_{11})_n^{6n-}$

(*a*) It is the formula of double chain silicate
(*b*) It is non-planar polymeric anion
(*c*) Each silicon is surrounded by 2.5 oxygen
(*d*) None of the above

16. $B_3N_3H_6$ + solution of hydrochloric acid ⟶ ?

Select CORRECT about above reaction.

(*a*) No reaction
(*b*) $B_3N_3H_6$ show substitution reaction and produce $B_3N_3Cl_6$
(*c*) $B_3N_3H_6$ show addition reaction and produce $B_3N_3H_9Cl_3$ in which Cl is bonded to boron
(*d*) $B_3N_3H_6$ show addition reaction and produce $B_3N_3H_9Cl_3$ in which Cl is bonded to nitrogen

17. Find the correct molar ratio of alkyl group, silicon and chlorine in alkyl substituted chloro silicon which is used as monomer in formation of cyclic silicones.

(*a*) 1 : 1 : 1
(*b*) 2 : 2 : 1
(*c*) 2 : 1 : 2
(*d*) 1 : 1 : 2

18. The SiO_2 molecule is formed by:

(*a*) Two σ overlapping as well as two π overlapping by each silicon atom
(*b*) One σ_{3s-2p} and one σ_{3p-2p} and two 2pπ–3pπ overlapping
(*c*) all the four σ overlapping using sp^3 hybridised orbitals of Si
(*d*) none of the above

19. The correct order of Lewis acid strengths of BF_2Cl, BFClBr, BF_2Br and $BFBr_2$ is:

(*a*) $BF_2Cl > BFClBr > BF_2Br > BFBr_2$
(*b*) $BFBr_2 > BFClBr > BF_2Br > BF_2Cl$
(*c*) $BF_2Cl > BF_2Br > BFClBr > BFBr_2$
(*d*) $BFClBr > BFBr_2 > BF_2Cl > BF_2Br$

Credit:--- Divansh.....

20. Anion $Si_3O_9^{x-}$ is present in benitoite (a barium titanium silicate mineral). Thus value of x is:

(*a*) 5 (*b*) 6

(*c*) 7 (*d*) 12

MULTIPLE CORRECT TYPE QUESTIONS

21. Which of the following facts regarding boron and silicon is/are true?
   (*a*) Boron is used to make boron steel or boron carbide control rods for nuclear reactor.
   (*b*) Boron and silicon form halides which are not hydrolysed.
   (*c*) Boron and silicon react with magnesium to form magnesium boride and magnesium silicide which are decomposed by acids to give volatile borane and silane, respectively.
   (*d*) Both boron and silicon react with alkali to form borates and silicates containing BO_3^{3-} and SiO_4^{4-} tetrahedral units, respectively.

22. Which among the following species does exist?
   (*a*) $[BF_6]^{3-}$ (*b*) $[AlF_6]^{3-}$ (*c*) $[GaF_6]^{3-}$ (*d*) $[InF_6]^{3-}$

23. Which of the following statement(s) is/are correct?
   (*a*) The oxide, B_2O_3 and hydroxide $B(OH)_3$ are acidic
   (*b*) The halides of B (except BF_3) and Si are readily hydrolysed.
   (*c*) The hydrides of B and Si are volatile, spontaneously flammable and readily hydrolysed.
   (*d*) Aluminium hydride is a polymer, $(AlH_3)_n$.

24. Which is/are the correct statement(s)?
   (*a*) BeF_2 readily coordinates two additional F^- ions forming the $[BeF_4]^{2-}$ complex.
   (*b*) One mole of borax in aqueous solution reacts with two moles of monobasic acid.
   (*c*) HCOONa as well as solid $K_4[Fe(CN)_6]$ both on heating with concentrated sulphuric acid evolve carbon monoxide gas.
   (*d*) Carbon mono oxide when passed through a solution of iodine pentaoxide, I_2O_5 liberates iodine and carbon dioxide.

25. Which of the following statements about anhydrous aluminium chloride is/are incorrect ?
   (*a*) It exists as $AlCl_3$ molecule in gaseous phase
   (*b*) It is a strong Lewis base
   (*c*) It sublimes at 100°C under vacuum
   (*d*) It is not easily hydrolysed

26. Select the correct statement(s)
   (*a*) The graphite is diamagnetic and diamond is paramagnetic in nature.
   (*b*) Graphite acts as a metallic conductor along the layers of carbon atoms and as semi-conductor perpendicular to the layers of the carbon atoms.
   (*c*) Graphite is less denser than diamond
   (*d*) C_{60} is called as Buckminster fullerene

27. Carbon monoxide is prepared by:
   (*a*) Heating formic acid with conc. H_2SO_4
   (*b*) Heating potassium ferrocyanide with conc H_2SO_4
   (*c*) Heating malonic acid with P_4O_{10}
   (*d*) Hydrolysis of Mg_2C_3

28. Which of the following statement(s) is/are false for soluble bicarbonates?
   (*a*) They give pink colour with phenolphthalein.
   (*b*) They do not liberate carbon dioxide with phenol.
   (*c*) They give white precipitate with magnesium nitrate in cold.
   (*d*) They liberate carbon dioxide on reaction with dil. H_2SO_4.

29. $Ca_2B_6O_{11} + Na_2CO_3 \xrightarrow{\Delta} [X] + CaCO_3 + NaBO_2$ (unbalanced equation)

   Correct choice(s) for [X] is/are:
   (*a*) structure of anion of crystalline [X] has one boron atom sp^3 hybridised and other three boron atoms sp^2 hybridised.
   (*b*) X with NaOH (aq.) gives a compound which on reaction with hydrogen peroxide in alkaline medium yields a compound used as bleaching agent in soaps.
   (*c*) hydrolysis of [X] with HCl or H_2SO_4 yields a compound which on reaction with HF gives fluoroboric acid
   (*d*) [X] on heating with chromium salts in oxidising flame gives green coloured bead in cold.

30. Identify the correct statements
   (*a*) Aqueous solution of one mole borax requires two moles of monobasic acid.
   (*b*) Boron nitride is slippery solid.
   (*c*) BBr_3 and BCl_3 both form complex with arsine (AsH_3) while BF_3 does not.
   (*d*) Although aluminium is above hydrogen in the electrochemical series yet it is stable in air and water.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 31 to 33): Compound (A) on reaction with iodine in the solvent diglyme gives a hydride (B) and hydrogen gas. The product (B) is instantly hydrolysed by water or aqueous alkali forming compound (C) and liberating hydrogen gas. The compound (C) in aqueous solution behaves as a weak mono basic acid. But in presence of certain organic polyhydroxy compound (C) behaves as a strong monobasic acid. The hydride (B) in air catches fire spontaneously forming oxide which gives coloured beads with transition metal compounds.

31. Which of the following statements is correct for the product (C)?
   (*a*) It is an odd electron molecule.
   (*b*) It acts as proton donor in water.
   (*c*) It has hydrogen bonding in solid state.
   (*d*) It is a useful primary standard for titration against acids.

32. Aqueous solution of product (C) can be titrated against sodium hydroxide using phenolphthalein indicator only in presence of:
   (*a*) cis-1, 2 diol (*b*) trans-1, 2 diol
   (*c*) borax (*d*) Na_2HPO_4

33. Which of the following statement is correct for hydride (B)?

(a) One mole of it react with two moles of HCl.

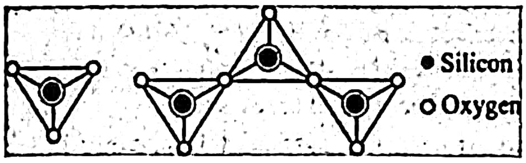
(b) It reacts with excess of ammonia at low temperature to form an ionic compound.

(c) One mole of it reacts with one mole of trimethylamine.

(d) It reacts with methyl alcohol to form a trimethyl compound liberating oxygen gas.

Comprehension (Q. 34 to 36): The name 'silica' covers an entire group of minerals, which have the general formula SiO_2, the most common of which is quartz. Quartz is a framework silicate with SiO_4 tetrahedral arranged in spirals. The spirals can turn in a clockwise or anticlockwise direction a feature that results in there being two mirror images, which are optically active varieties of quartz.

34. The following pictures represent various silicate anions. Their formulae are respectively

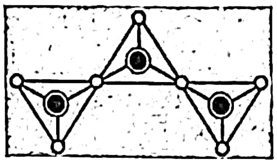


(a) $SiO_3^{2-}, Si_3O_7^{2-}$ (b) $SiO_4^{4-}, Si_3O_{10}^{8-}$

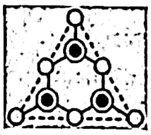
(c) $SiO_4^{2-}, Si_3O_9^{2-}$ (d) $SiO_3^{4-}, Si_3O_7^{8-}$

35. $Si_3O_9^{6-}$ (having three tetrahedral) is represented as:

(a)



(b)



(c) Both (a) and (b)

(d) None of these

36. The silicate anion in the mineral kinolite is a Chain of three SiO_4 tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca^{2+} ions, Cu^{2+} ions and water molecule in a 1 : 1 : 1 ratio. The mineral is represented as:

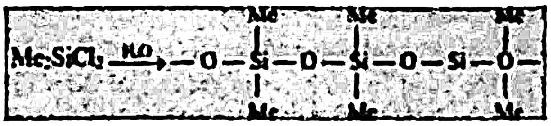
(a) $CaCuSi_3O_{10}.H_2O$ (b) $CaCuSi_3O_{10}.2H_2O$

(c) $Ca_2Cu_2Si_3O_{10}.2H_2O$ (d) None of these

Comprehension (Q. 37 to 38): Read the following write-ups and answer the questions at the end of it.

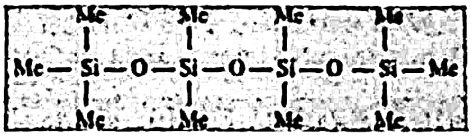
Silicones are synthetic polymers containing represented R_2SiO units. Since, the empirical formula is that of a ketone (R_2CO) the name silicone has been given to these. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of R_2SiCl_2 [R = methyl (Me) or phenyl (ϕ)]

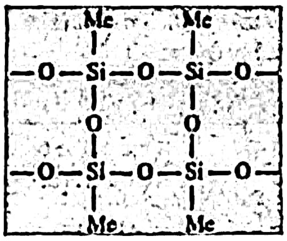


37. If we mix Me_3SiCl with Me_2SiCl_2, we get silicones of the type:

(a)



(b)

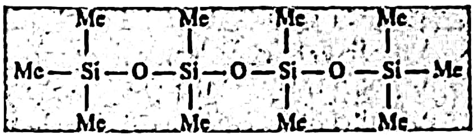


(c) Both of the above

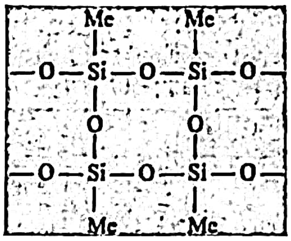
(d) None of the above

38. If we start with $MeSiCl_3$ as the starting material, silicone formed is:

(a)



(b)



(c) Both of the above

(d) None of the above

Comprehension (Q. 39 to 41): Compound (A) on reduction with $LiAlH_4$ gives a hydride (P) containing 21.72% hydrogen along with other products. The one mole of hydride (P) and 2 mole of ammonia at higher temperature gives a compound (Q) which is known as inorganic benzene. (A) hydrolyses incompletely and forms a compound (R) and H_3BO_3.

39. In hydride (P) (select correct statement):

(a) The central atom has trigonal planar geometry

(b) All H-atoms lie in the same plane.

(c) All four terminal B-H bond lengths are equivalent but that of four bridging B-H bond lengths are not equivalent.

(d) A three-centre two-electron bond (3c - 2e) is formed by overlap of an sp^3 hybrid orbital from each boron atom with the 1s orbital of hydrogen atom.

Credit:--- Divansh.....

40. The hybridisation of central atom of compound (R) is:

(*a*) sp^2 (*b*) sp^3 (*c*) sp (*d*) sp^3d

41. Which of the following statement is incorrect for the compound (A)?

(*a*) It has trigonal planar geometry.

(*b*) The bond length between the central atom and the substituent atoms is shorter than the sum of the covalent radii.

(*c*) The coordination geometry around central atom of compound (A) and N atom in 1 : 1 complex of (A) and NH_3 is same.

(*d*) In compound (A), there is pπ-dπ bonding.

MATCH THE COLUMN TYPE QUESTIONS

42. Match the reactions listed in column-I with characteristic(s)/ type of reactions listed in column-II.

Column-I		Column-II	
A.	$Al_2(C_2)_3 + H_2O \rightarrow$	p.	One of the products contains both σ and π bonds
B.	$CH_2(COOH)_2 + P_4O_{10} \rightarrow$	q.	Hydrolysis
C.	$CH_3SiCl_3 + H_2O \rightarrow$	r.	Dehydration
D.	$SnCl_2.2H_2O \xrightarrow[\text{standing}]{\text{on}}$	s.	Complex crosslinked polymer

(*a*) A-(p); B-(p,r); C-(r,s); D-(q)

(*b*) A-(p,q); B-(p,r); C-(q,s); D-(q)

(*c*) A-(p,q); B-(q,s); C-(p,r); D-(r)

(*d*) A-(r); B-(p,s); C-(q,s); D-(p)

43. Match the reactions listed in column-I with characteristic(s)/ type of reactions listed in column-II.

Column-I		Column-II	
A.	$BBr_3 + H_2 \longrightarrow B$	p.	Borax bead test
B.	$Na_2B_4O_7.10H_2O + CuSO_4 \rightarrow Cu(BO_2)_2$	q.	Reduction
C.	$AlCl_3 + H_2O \longrightarrow HCl$	r.	White fumes
D.	$Cr_2O_3 + Al \longrightarrow Cr$	s.	Hydrolysis

(*a*) A-(p,s); B-(q,r); C-(r); D-(p)

(*b*) A-(p,q); B-(q); C-(s); D-(q)

(*c*) A-(q); B-(p); C-(r,s); D-(q)

(*d*) A-(p); B-(q,r); C-(r,p); D-(r)

INTEGER TYPE QUESTIONS

44. For Boron family (B, Al, Ga, In and Tl)

x : Number of elements which are solid at 40°C.

y : Period number of element which has greater ionization energy than element just above and below it in periodic table.

z : Period number of most abundant element of group 13.

Report your answer as value of x + 2y + 3z

45. Consider a prototypical fullerene, C_{60}.

Let, a = Number of 5-membered rings

b = Number of 6-membered rings

c = Number of π-bonds in C_{60}

Find the value of (3a – 2b + c)

46. $B_{10}C_2H_{12}$ is isostructural & isoelectronic with borate ion of formula $B_xH_y^{z-}$ find value of x + y + z.

47. (*a*) Number of ions which are regarded as ionic carbides amongst

$(C^{4-}, C_2^{2-}, C_3^{4-}, C_4^{3-}) = X$

(*b*) When oxalic acid is heated with conc. H_2SO_4 it produces, number of different gases amongst

$(CO, CO_2, SO_3) = Y$

(*c*) Number of molecules having V-shaped structure amongst

$(SnCl_2, PbCl_2, COS) = Z$

Find the value of X + Y + Z

48. In the compound $Na_2[B_4O_5(OH)_4]\cdot8H_2O$, if the

(*i*) Number of B—O—B bonds is '*x*'

(*ii*) Number of B—B bonds is '*y*'

(*iii*) Number of sp^2 hybridized B atoms is '*z*'

Calculate the value of *x* + *y* + *z*.

49. Find the difference between total number of lone pairs and total number of σ-bonds in $[B_3O_3(OH)_6]^{3-}$ molecular ion:

50. Consider the structure of Al_2Me_6 compound and find the value of $\frac{x-y}{z}$.

Where *x* = Maximum number of atoms that can lie in plane having terminal (Al – Me) bonds.

y = Total number of $3c - 2e^-$ bonds.

z = Total number of atoms that are sp^3 hybridized

51. Consider $Al_2(OH)_6$ compound and calculate the value of (X + Y) ÷ Z.

Where X = Total number of $(2c - 2e^-)$ bond.

Y = Total number of $(3c - 2e^-)$ bond

Z = Total number of $(3c - 4e^-)$ bond

52. When SnC_2O_4 is heated in absence of air, find the difference in oxidation states of carbon atoms in gaseous products.

53. $SiCl_4 \xrightarrow{H_2O} X \xrightarrow{1000°C} Y$

In the above reaction, how many oxygen atom(s) is/are present per molecule of X and Y?

[If answer is 6 and 4, represent as 64]

54. $R_nSiCl_{(4-n)}$ on hydrolysis and followed by condensation polymerisation yields straight chain polymers. Find the value of n.

55. Find the number of compounds from the following with which diborane cleaves unsymmetrically forming $[L_2H_2B]^+[BH_4]^-$ type of complex.

NH_3, Et_3N, Et_2NH, $EtNH_2$, CO, tetrahydrofuran

Credit:--- Divansh.....

PYQ's (Past Year Questions)

GROUP 13 ELEMENTS : THE BORON FAMILY

1. Given below are two statements: One is labelled as **Assertion (A)** and the other is labelled as **Reason (R).**

Assertion (A): Melting point of Boron (2453 K) is unusually high in group 13 elements.

Reason (R): Solid Boron has very strong crystalline lattice.

In the light of the above statements, choose the most appropriate answer from the options given below:

[27 Jan, 2024 (Shift-I)]

(*a*) Both (A) and (R) are correct but (R) Is not the correct explanation of (A)

(*b*) Both (A) and (R) are correct and (R) is the correct explanation of (A)

(*c*) (A) is true but (R) is false

(*d*) (A) is false but (R) is true

2. Aluminium chloride in acidified aqueous solution forms an ion having geometry **[30 Jan, 2024 (Shift-I)]**

(*a*) Octahedral (*b*) Square Planar

(*c*) Tetrahedral (*d*) Trigonal bipyramidal

3. Given below are two statements:

Statement-I: Group 13 trivalent halides get easily hydrolyzed by water due to their covalent nature.

Statement-II: $AlCl_3$ upon hydrolysis in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion.

In the light of the above statements, choose the correct answer from the options given below:

[31 Jan, 2024 (Shift-II)]

(*a*) Statement-I is true but statement-II is false

(*b*) Statement-I is false but statement-II is true

(*c*) Both statement-I and statement-II are false

(*d*) Both statement-I and statement-II are true

4. Given below are two statements:

Statement-I: In group 13, the stability of +1 oxidation state increases down the group.

Statement-II: The atomic size of gallium is greater than that of aluminium.

In the light of the above statements, choose the most appropriate answer from the options given below:

[05 April, 2024 (Shift-I)]

(*a*) Statement-I is incorrect but Statement-II is correct

(*b*) Both Statement-I and Statement-II are correct

(*c*) Both Statement-I and Statement-II are incorrect

(*d*) Statement-I is correct but Statement-II is incorrect

5. The correct statements from the following are:

(A) The decreasing order of atomic radii of group 13 elements is Tl > In > Ga > Al > B.

(B) Down the group 13 electronegativity decreases from top to bottom.

(C) Al dissolves in dil. HCl and liberate H_2 but conc. HNO_3 renders Al passive by forming a protective oxide layer on the surface.

(D) All elements of group 13 exhibits highly stable +1 oxidation state.

(E) Hybridisation of Al in $[Al(H_2O)_6]^{3+}$ ion is sp^3d^2.

Choose the correct answer from the options given below:

[05 April, 2024 (Shift-II)]

(*a*) (C) and (E) only

(*b*) (A), (C) and (E) only

(*c*) (A), (B), (C) and (E) only

(*d*) (A) and (C) only

6. Given below are two statements:

Statement-I: Gallium is used in the manufacturing of thermometers.

Statement-II: A thermometer containing gallium is useful for measuring the freezing point (256 K) of brine solution.

In the light of the above statement, choose the correct answer from the options given below: **[06 April, 2024 (Shift-I)]**

(*a*) Both Statement-I and Statement-II are false.

(*b*) Statement-I is false but Statement-II is true.

(*c*) Both Statement-I and Statement-II are true.

(*d*) Statement-I is true but Statement-II is false.

7. Given below are two statements: One is labelled as **Assertion (A)** and the other is labelled as **Reason (R):**

Assertion (A): The stability order of +1 oxidation state of Ga, In and Tl is Ga < In < Tl.

Reason (R): The inert pair effect stabilizes the lower oxidation state down the group.

In the light of the above statements, choose the correct answer from the options given below:

[08 April, 2024 (Shift-I)]

(*a*) Both (A) and (R) are true and (R) is the correct explanation of (A).

(*b*) (A) is true but R is false.

(*c*) Both (A) and (R) are true but (R) is NOT the correct explanation of (A).

(*d*) (A) is false but (R) is true.

8. Match List-I with List-II

List-I		List-II	
A.	Melting point [K]	I.	Tl > In > Ga > Al > B
B.	Ionic Radius $[M^{+3}/pm]$	II.	B > Tl > Al ≈ Ga > In
C.	$\Delta_i H_1$ [kJ mol^{-1}]	III.	Tl > In > Al > Ga > B
D.	Atomic Radius [pm]	IV.	B > Al > Tl > In > Ga

Choose the correct answer from the options given below:

[09 April, 2024 (Shift-II)]

(*a*) A-III, B-IV, C-I, D-II (*b*) A-II, B-III, C-IV, D-I

(*c*) A-IV, B-I, C-II, D-III (*d*) A-I, B-II, C-III, D-IV

9. Given below are two statements:

Statement-I: Boron is extremely hard indicating its high lattice energy

Statement-II: Boron has highest melting and boiling point compared to its other group members.

[12 April, 2023 (Shift-I)]

In the light of the above statements, choose the most appropriate answer from the options given below:

(*a*) Statement-I is incorrect but Statement-II is correct

(*b*) Both Statement-I and Statement-II is correct

(*c*) Statement-I is correct but Statement-II is incorrect

(*d*) Both Statement-I and Statement-II is incorrect

10. Given below are two statements. One is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**

Assertion (A): Boron is unable to form BF_6^{3-}

Reason (R): Size of B is very small.

[27 July, 2022 (Shift-II)]

In the light of the above statements, choose the correct answer from the options given below:

(*a*) Both (A) and (R) are true and (R) is the correct explanation of (A)

(*b*) Both (A) and(R) are true and (R) is NOT the correct explanation of (A)

(*c*) (A) is true but (R) is false

(*d*) (A) is false but (R) is true

11. Given below are two statements.

Statement-I: The chlorides of Be and Al have Cl-bridged structure. Both are soluble in organic solvents and act as Lewis bases.

Statement-II: Hydroxides of Be and Al dissolve in excess alkali to give beryllate and aluminate ions.

In the light of the above statements, choose the correct answer from the options given below.

[27 July, 2022 (Shift-I)]

(*a*) Both Statement-I and Statement-II are true.

(*b*) Both Statement-I and Statement-II are false.

(*c*) Statement-I is true but Statement-II is false.

(*d*) Statement-I is false but Statement-II is true.

12. Given below are two statements : one is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**.

Assertion (A): In TlI_3, isomorphous to CsI_3, the metal is present in +1 oxidation state.

Reason (R): Tl metal has fourteen f electrons in the electronic configuration. [26 Feb, 2021 (Shift-II)]

In the light of the above statements, choose the most appropriate answer from the options given below:

(*a*) (A) is correct but (R) is not correct

(*b*) Both (A) and (R) are correct but (R) is NOT the correct explanation of (A)

(*c*) (A) is not correct but (R) is correct

(*d*) Both (A) and (R) are correct and (R) is the correct explanation of (A)

13. Match List-I with List-II:

	List-I		List-II
A.	NaOH	(I)	Acidic
B.	$Be(OH)_2$	(II)	Basic
C.	$Ca(OH)_2$	(III)	Amphoteric
D.	$B(OH)_3$		
E.	$Al(OH)_3$		

Choose the most appropriate answer from the options given below: [27 July, 2021 (Shift-I)]

(*a*) (A)-(II), (B)-(I), (C)-(II), (D)-(III), (E)-(III)

(*b*) (A)-(II), (B)-(III), (C)-(II), (D)-(I), (E)-(III)

(*c*) (A)-(II), (B)-(II), (C)-(III), (D)-(II), (E)-(III)

(*d*) (A)-(II), (B)-(II), (C)-(III), (D)-(I), (E)-(III)

14. In which one of the following molecules, strongest back donation of an electron pair from halide to boron is expected?

[27 Aug, 2021 (Shift-I)]

(*a*) BBr_3 (*b*) BF_3 (*c*) BCl_3 (*d*) BI_3

15. The correct statements among I to III regarding group 13 element oxides are [9 April, 2019 (Shift-II)]

(I) Boron trioxide is acidic.

(II) Oxides of aluminium and gallium are amphoteric.

(III) Oxides of indium and thallium are basic.

(*a*) (I), (II) and (III) (*b*) (II) and (III) only

(*c*) (I) and (III) only (*d*) (I) and (II) only

16. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to

[9 Jan, 2019 (Shift-I)]

(*a*) Inert pair effect (*b*) diagonal relationship

(*c*) Lattice effect (*d*) Lanthanoid contraction

SOME IMPORTANT COMPOUNDS OF GROUP-13 ELEMENTS

17. The number of neutrons present in the most abundant isotope of boron is 'x'. Amorphous boron upon heating with air forms a product, in which the oxidation state of boron is 'y'. The value of $x + y$ is ... [05 April, 2024 (Shift-I)]

(*a*) 4 (*b*) 6 (*c*) 3 (*d*) 9

18. Lithium aluminium hydride can be prepared from the reaction of [30 Jan, 2023 (Shift-I)]

(*a*) LiCl and Al_2H_6 (*b*) LiH and Al_2Cl_6

(*c*) LiCl, Al and H_2 (*d*) LiH and $Al(OH)_3$

19. Boric acid is solid, whereas BF_3 is gas at room temperature because of [30 Jan, 2023 (Shift-II)]

(*a*) Strong ionic bond in Boric acid

(*b*) Strong van der Waal's interaction in Boric acid

(*c*) Strong hydrogen bond in Boric acid

(*d*) Strong covalent bond in BF_3

20. Given below are two statements:

Statement-I: Upon heating a borax bead dipped in cupric sulphate in a luminous flame, the colour of the bead becomes green.

Statement-II: The green colour observed is due to the formation of copper(I) metaborate.

[31 Jan, 2023 (Shift-II)]

In the light of the above statements, choose the most appropriate answer from the options given below:

(*a*) Both Statement-I and Statement-II are true

(*b*) Statement-I is true but Statement-II is false

(*c*) Both Statement-I and Statement-II are false

(*d*) Statement-I is false but Statement-II is true

21. If the formula of Borax is $Na_2B_4O_x(OH)_y \cdot zH_2O$, then $x + y + z =$ [13 April, 2023 (Shift-II)]

22. When borax is heated with CoO on a platinum loop, blue coloured bead formed is largely due to

[29 July, 2022 (Shift-II)]

(*a*) B_2O_3 (*b*) $Co(BO_2)_2$

(*c*) CoB_4O_7 (*d*) $Co[B_4O_5(OH)_4]$

23. Identify the correct statement for B_2H_6 from those given below: [24 June, 2022 (Shift-I)]

(A) In B_2H_6, all B-H bonds are equivalent

(B) In B_2H_6, there are four 3- centre 2- electron bonds

(C) B_2H_6 is a Lewis acid

(D) B_2H_6 can be synthesized from both BF_3 and $NaBH_4$

(E) B_2H_6 is planar molecule

Choose the most appropriate answer from the options given below:

(*a*) (A) and (E) only

(*b*) (B), (C) and (E) only

(*c*) (C) and (D) only

(*d*) (C) and (E) only

24. Aqueous solution of which of the following boron compounds will be strongly basic in nature?

[29 June, 2022 (Shift-II)]

(*a*) $NaBH_4$ (*b*) $LiBH_4$

(*c*) B_2H_6 (*d*) $Na_2B_4O_7$

25. Given below are the statements about diborane.

(A) Diborane is prepared by the oxidation of $NaBH_4$ With I_2.

(B) Each boron atom is in sp^2 hybridized state.

(C) Diborane has one bridged 3 centre – 2 – electron bond.

(D) Diborane is a planar molecule.

The option with correct statement(s) is:

[22 July, 2021 (Shift-II)

(*a*) (A) only (*b*) (C) only

(*c*) (A) and (B) only (*d*) (C) and (D) only

26. The correct statement about B_2H_6 is:

[25 Feb, 2021 (Shift-I)]

(*a*) All B – H – B angles are of 120°.

(*b*) The two B – H – B bonds are not of same length.

(*c*) Its fragment, BH_3, behaves as a Lewis base.

(*d*) Terminal B – H bonds have less p – character when compared to bridging bonds.

27. The reaction of $H_3N_3B_3Cl_3$(A) with $LiBH_4$ in tetrahydrofuran gives inorganic benzene (B).

Further, the reaction of (A) with (C) leads to $H_3N_3B_3(Me)_3$. Compounds (B) and (C) respectively, are:

[9 Jan, 2020 (Shift-II)]

(*a*) Borazine and MeBr

(*b*) Boron nitride and MeBr

(*c*) Diborane and MeMgBr

(*d*) Borazine and MeMgBr

28. Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively **[8 April, 2019 (Shift-I)]**

(*a*) HBO_2 and H_3BO_3 (*b*) H_3BO_3 and B_2O_3

(*c*) B_2O_3 and H_3BO_3 (*d*) B_2O_3 and $[BH_4]$

GROUP 14 ELEMENTS : THE CARBON FAMILY

29. Given below are two statements:

Statement-I: The electronegativity of group 14 elements from Si to Pb gradually decreases.

Statement-II: Group 14 contains non-metallic, metallic, as well as metalloid elements.

In the light of the above statements, choose the most appropriate from the options given below:

[29 Jan, 2024 (Shift-I)]

(*a*) Statement-I is false but Statement-II is true

(*b*) Statement-I is true but Statement-II is false

(*c*) Both Statement-I and Statement-II are true

(*d*) Both Statement-I and Statement-II are false

30. Consider the oxides of group 14 elements

SiO_2, GeO_2, SnO_2, PbO_2, CO and GeO. The amphoteric oxides are **[31 Jan, 2024 (Shift-I)]**

(*a*) GeO, GeO_2 (*b*) SiO_2, GeO_2

(*c*) SnO_2, PbO_2 (*d*) SnO_2, CO

31. Which of the following material is not a semiconductor.

[06 April, 2024 (Shift-I)]

(*a*) Germanium (*b*) Graphite

(*c*) Silicon (*d*) Copper oxide

32. The number of ions from the following that are expected to behave as oxidising agent is: **[06 April, 2024 (Shift-II)]**

Sn^{4+}, Sn^{2+}, Pb^{2+}, Tl^{3+}, Pb^{4+}, Tl^{+}

(*a*) 3 (*b*) 4

(*c*) 1 (*d*) 2

Credit:--- Divansh.....

33. Evaluate the following statements related to group 14 elements for their correctness. **[06 April, 2024 (Shift-II)]**

(A) Covalent radius decreases down the group from C to Pb in a regular manner.

(B) Electronegativity decreases from C to Pb down the group gradually.

(C) Maximum covalence of C is 4 whereas other elements can expand their covalence due to presence of d orbitals.

(D) Heavier elements do not form pπ-pπ bonds.

(E) Carbon can exhibit negative oxidation states.

Choose the correct answer from the options given below:

(*a*) (C), (D) and (E) Only

(*b*) (A) and (B) Only

(*c*) (A), (B) and (C) Only

(*d*) (C) and (D) Only

34. The compound which does not exist is **[10 April, 2023 (Shift-I)]**

(*a*) Na_2O_2 (*b*) $(NH_4)_2BeF_4$

(*c*) BeH_2 (*d*) $PbEt_4$

35. The stoichiometric reaction of 516 g of dimethyl dichlorosilane with water results in a tetrameric cyclic product X in 75% yield. The weight (in g) of X obtained is___.

[Use, molar mass (g mol^{-1}): H = 1, C = 12, O = 16, Si = 28, Cl = 35.5] **[JEE Adv 2023]**

36. Given below are two statements.

Statement-I: Stannane is an example of a molecular hydride.

Statement-II: Stannane is a planar molecule.

In the light of the above statement, choose the *most appropriate* answer from the options given below. **[29 July, 2022 (Shift-I)]**

(*a*) Both statement-I and Statement-II are true.

(*b*) Both statement-I and Statement-II are false.

(*c*) Statement-I is true but Statement-II is false.

(*d*) Statement-I is false but Statement-II is true.

37. Match the List-I with List-II.

List-I (Metal)		List-II (Application)	
A.	Cs	(I)	High temperature thermometer
B.	Ga	(II)	Water repellent sprays
C.	B	(III)	Photoelectric cells
D.	Si	(IV)	Bullet proof vest

Choose the most appropriate answer from the options given below: **[29 June, 2022 (Shift-I)]**

(*a*) (A)-(III), (B)-(I), (C)-(IV), (D)-(II)

(*b*) (A)-(IV), (B)-(III), (C)-(II), (D)-(I)

(*c*) (A)-(II), (B)-(III), (C)-(IV), (D)-(I)

(*d*) (A)-(I), (B)-(IV), C)-(II), (D)-(III)

38. Ge (Z = 32) in its ground state electronic configuration has x completely filled orbitals with $m_\ell = 0$. The value of x is _______. **[31 Aug, 2021 (Shift-I)]**

39. The correct statement among the following is **[12 April, 2019 (Shift-I)]**

(*a*) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$

(*b*) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$

(*c*) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$

(*d*) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$

40. Correct statements among (i) to (iv) regarding silicones are

(*i*) They are polymers with hydrophobic character

(*ii*) They are biocompatible

(*iii*) In general, they have high thermal stability and low dielectric strength

(*iv*) Usually they are resistant to oxidation and used as greases. **[9 Jan, 2019 (Shift-I)]**

(*a*) (*i*), (*ii*), (*iii*) and (*iv*) (*b*) (*i*), (*ii*) and (*iii*)

(*c*) (*i*) and (*ii*) only (*d*) (*i*), (*ii*) and (*iv*)

41. Choose the correct statement(s) among the following. **[JEE Adv 2020]**

(*a*) $SnCl_2.2H_2O$ is a reducing agent

(*b*) SnO_2 reacts with KOH to form $K_2[Sn(OH)_6]$

(*c*) A solution of $PbCl_2$ in HCl contains Pb^{2+} and Cl^- ions

(*d*) The reaction of Pb_3O_4 with hot dilute nitric acid to give PbO_2 is a redox reaction

ALLOTROPES OF CARBON

42. Given below are two statements:

Statement-I: SiO_2 and GeO_2 are acidic while SnO and PbO are amphoteric in nature.

Statement-II: Allotropic forms of carbon are due to property of catenation and pπ-dπ bond formation.

In the light of the above statements, choose the most appropriate answer from the options given below: **[01 Feb, 2024 (Shift-II)]**

(*a*) Both Statement-I and Statement-II are false

(*b*) Both Statement-I and Statement-II are true

(*c*) Statement-I is true but Statement-II is false

(*d*) Statement-I is false but Statement-II is true

43. The INCORRECT statement regarding the structure of C_{60} is: **[16 March, 2021 (Shift-II)]**

(*a*) Each carbon atom forms three sigma bonds

(*b*) The five-membered rings are fused only to six-membered rings

(*c*) The six-membered rings are fused to both six and five-memebered rings

(*d*) It contains 12 six-membered rings and 24 five-membered rings

44. The C–C bond length is maximum in **[12 April, 2019 (Shift-II)]**

(*a*) Graphite (*b*) C_{70}

(*c*) Diamond (*d*) C_{60}

SOME IMPORTANT COMPOUNDS OF CARBON & SILICON

45. Given below are two statements, one is labelled as **Assertion (A)** and the other is labelled as **Reason (R)**.

Assertion (A): Carbon forms two important oxides –CO and CO_2.CO is neutral whereas CO_2 is acidic in nature.

Reason (R): CO_2 can combine with water in a limited way to form carbonic acid, while CO is sparingly soluble in water.

In the light of the above statements, choose the most appropriate answer from the options given below:

[25 Jan, 2023 (Shift-II)]

(*a*) Both (A) and (R) are correct but (R) is NOT the correct explanation of (A).

(*b*) Both (A) and (R) are correct and (R) is the correct explanation of (A).

(*c*) (A) is not correct but (R) is correct.

(*d*) (A) is correct but (R) is not correct.

46. Match the List-I with List-II.

	List- I (Si-Compounds)		List- II (Si-polymeric/Other Products)
A.	$(CH_3)_4Si$	(I)	Chain Silicone
B.	$(CH_3)Si(OH)_3$	(II)	Dimeric Silicone
C.	$(CH_3)_2Si(OH)_2$	(III)	Silane
D.	$(CH_3)_3Si(OH)$	(IV)	2D-Silicon

[27 June, 2022 (Shift-I)]

(*a*) (A)-(III), (B)-(II), (C)-(I), (D)-(IV)

(*b*) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)

(*c*) (A)-(II), (B)-(I), (C)-(IV), (D)-(III)

(*d*) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

PW Challengers

PASSAGE I

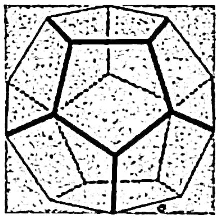
From 20 mg of partially methylated disilane, $Si_2H_{6-x}(CH_3)_x$, 27.8 cm^3 of hydrogen are evolved during alkaline hydrolysis at 294 K and 97400 Pa.

1. Calculate the degree of substitution x of the methylated disilane. **(Integer Type)**
2. How many isomers of disilane can form the calculated compound? **(Integer Type)**

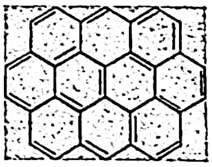
PASSAGE II

The three-dimensional structures of polycyclic molecules can often be explained in terms of the minimisation of angle strain. Consider the following molecules:

Dodecahedrane, $C_{20}H_{20}$



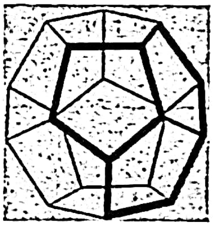
and Ovalene, $C_{32}H_{14}$.



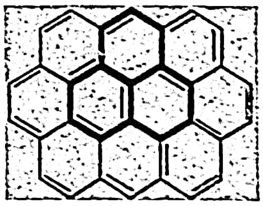
Each C_5 ring of dodecahedrane is a regular pentagon, while each C_6 ring of ovalene can be regarded as a regular hexagon.

3. What are the ∠ (CCC) angles (in degrees)for each of these rings?

4. A "juncture" is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctures (shown in bold) of three pentagons within dodecahedrane:

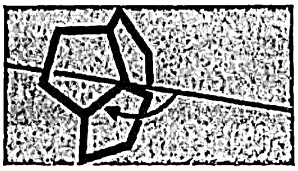


and of three hexagons within ovalene:



Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.

Credit:--- Divansh.....

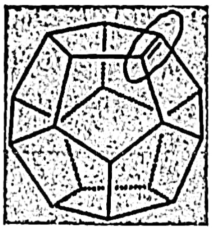


What is the value of this angle (in degrees)for dodecahedran, and for ovalene?

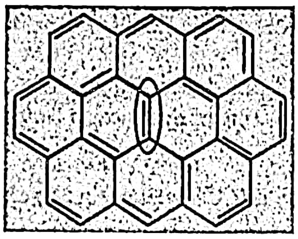
5. Subtracting 90° from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar?

   (A) Dodecahedrane, (B) Ovalene

6. Now consider two polycyclic 'alkenes', dodecahedrene ($C_{20}H_{18}$):



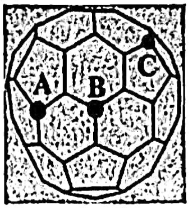
and ovalene:



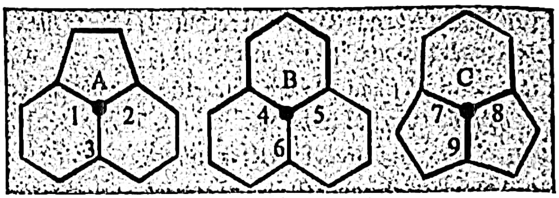
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

Compare the indicated pairs of carbon atoms (encircled above). For which C=C pair, is H_2 addition expected to be more exothermic?

7. There is evidence for fullerenes smaller than C_{60}, such as C_{58}. The C_{58} structure (ignoring any distinction between 'double' and 'single' bonds) is shown below:



The junctures centred on atoms A, B and C on the above structure can be redrawn for greater clarity:

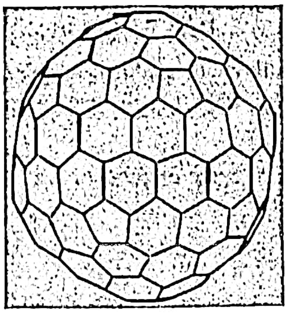


Which juncture has the least deviation from planarity?

8. Which juncture has the greatest deviation from planarity?

9. Of the above carbon-carbon bonds, numbered from 1 to 9, which represents the most favourable site for H_2 addition? **(Integer Type)**

10. Finally, consider a larger fullerene, C_{180}:



To a first approximation, both C_{60} and C_{180} are "perfect" spheres. Which has the larger average deviation from planarity at each juncture? C_{60} or C_{180}?

NATURE CARE ROUTINE

- Plant a tree or tend to a garden, focusing on the texture of the soil, the smell of the plants, and the sounds of nature.
- Reflect on how your actions contribute to a healthier environment, fostering a deeper connection with nature and a sense of responsibility for its well-being.

Credit:--- Divansh.....

ANSWER KEY

CONCEPT APPLICATION

1. (*b*) 2. (*a*) 3. (c) 4. (*b*) 5. (*c*) 6. (*c*) 7. (*b*) 8. (*c*) 9. (*c*) 10. (*c*)
11. (*c*) 12. (*c*) 13. (*b*) 14. (*a*) 15. (*c*) 16. (*d*) 17. (*c*) 18. (*d*) 19. (*b*) 20. (*d*)
21. (*d*) 22. (*a*) 23. (*a*) 24. (*a*) 25. (*a*) 26. (*a*) 27. (*c*) 28. (*c*) 29. (*c*) 30. (*a*)

SCHOOL LEVEL PROBLEMS

1. (*d*) 2. (*c*) 3. (*a*) 4. (*c*) 5. (*c*) 6. (*c*) 7. (*b*) 8. (*a*) 9. (*b*) 10. (*a*)
11. (*d*) 12. (*b*) 24. (i)-(*b*), (ii)-(*d*), (iii)-(*c*), (iv)-(*b*)

PRARAMBH (TOPICWISE)

1. (*b*) 2. (*c*) 3. (*b*) 4. (*b*) 5. (*a*) 6. (*b*) 7. (*a*) 8. (*a*) 9. (*c*) 10. (*a*)
11. (*b*) 12. (*c*) 13. (*b*) 14. (*c*) 15. (*a*) 16. (*a*) 17. (*b*) 18. (*c*) 19. (*a*) 20. (*c*)
21. (*b*) 22. (*c*) 23. (*b*) 24. (*c*) 25. (*c*) 26. (*c*) 27. (*a*) 28. (*a*) 29. (*d*)

PRABAL (JEE MAIN LEVEL)

1. (*b*) 2. (*d*) 3. (*d*) 4. (*a*) 5. (*d*) 6. (*d*) 7. (*c*) 8. (*d*) 9. (*b*) 10. (*d*)
11. (*a*) 12. (*b*) 13. (*d*) 14. (*a*) 15. (*b*) 16. (*a*) 17. (*a*) 18. (*c*) 19. (*c*) 20. (*d*)
21. (*c*) 22. (*b*) 23. (*b*) 24. (*d*) 25. (*b*) 26. (*c*) 27. (*b*) 28. (*b*) 29. (*b*) 30. (*d*)
31. (*b*) 32. (*b*) 33. [6] 34. [6] 35. [7] 36. [5] 37. [5] 38. [6] 39. [2] 40. [2]

PARIKSHIT (JEE ADVANCED LEVEL)

1. (*c*) 2. (*d*) 3. (*c*) 4. (*a*) 5. (*a*) 6. (*c*) 7. (*c*) 8. (*d*) 9. (*b*) 10. (*a*)
11. (*d*) 12. (*a*) 13. (*b*) 14. (*c*) 15. (*c*) 16. (*c*) 17. (*c*) 18. (*c*) 19. (*b*) 20. (*b*)
21. (*a,c,d*) 22. (*b,c,d*) 23. (*a,b,c,d*) 24. (*a,b,c,d*) 25. (*a,b,d*) 26. (*b,c,d*) 27. (*a,b*) 28. (*a,c*) 29. (*b,c,d*)
30. (*a,b,c,d*) 31. (*c*) 32. (*a*) 33. (*b*) 34. (*b*) 35. (*b*) 36. (*c*) 37. (*a*) 38. (*b*) 39. (*d*)
40. (*b*) 41. (*d*) 42. (*b*) 43. (*c*) 44. [21] 45. [26] 46. [26] 47. [7] 48. [7] 49. [0]
50. [1] 51. [5] 52. [2] 53. [42] 54. [2] 55. [3]

PYQ's (PAST YEAR QUESTIONS)

1. (*b*) 2. (*a*) 3. (*d*) 4. (*d*) 5. (*a*) 6. (*d*) 7. (*a*) 8. (c) 9. (*b*) 10. (*b*)
11. (*d*) 12. (*b*) 13. (*b*) 14. (*b*) 15. (*a*) 16. (*a*) 17. (*d*) 18. (*b*) 19. (*c*) 20. (*c*)
21. [17] 22. (*b*) 23. (*c*) 24. (*d*) 25. (*a*) 26. (*d*) 27. (*d*) 28. (*b*) 29. (*a*) 30. (*c*)
31. (*b*) 32. (*d*) 33. (*a*) 34. (*a*) 35. [222] 36. (*c*) 37. (*a*) 38. [7] 39. (*d*) 40. (*d*)
41. (*a,b,c*) 42. (*c*) 43. (*d*) 44. (*c*) 45. (*b*) 46. (*d*)

PW CHALLENGERS

1. [2] 2. [2] 3. [108,120] 4. [109-115,90] 5. [B] 6. [dodecahedrene, $C_{20}H_{18}$]
7. (B) 8. (C) 9. [9] 10. [C_{60}]